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RESEARCH ON THE ELECTRO- CHEMICAL OXIDATION OF HEXANE AND ITS ISOMERS

Seventh Semiannual Interim Report

Covering Period

November 16, 1968 - May 15, 1969

Contract No. DA 44-009-AMC-1408(T)

Prepared by

S. B. Brummer

M. J. Turner

Prepared for

U. S. Army Mobility Equipment
Research and Development
Center
Fort Belvoir, Virginia

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1T061102A34A00 009 EF

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ABSTRACT

The oxidation of CH_4 on Pt electrodes in 80% H_3PO_4 at 130°C has been studied. Emphasis has been put on the development of non-noble metal catalysts. To prevent corrosion the approach has been to stabilize these catalysts by adsorption.

Studies were made of the adsorption of Cu from solutions containing Cu^{++} . Cu adsorption on Pt is controlled by the rate of diffusion of Cu^{++} to the Pt electrode. Appreciable steady state coverage of Cu is found at potentials anodic to the reversible potential for the Cu^{++}/Cu reaction, proving that adsorption of Cu does occur. Maximum adsorption (about 0.8 of a monolayer) is found at about 0.20v vs. the reversible hydrogen electrode (RHE), with a slow decline to zero coverage at $\sim 0.60\text{v}$. The effect of Cu^{++} concentration on the coverage is most marked in the lower potential range from 0.10 to 0.35v.

Comparisons of the charge to oxidize the Cu layer, Q , with its coverage, θ , allow evaluation of the number of electrons released per site when the layer is oxidized, $[e]$. It is found that the $[e]$ value for the first half of the monolayer coverage is 1.8 electrons per site independent of potential. This corresponds closely to the value expected for the oxidation to Cu^{++} of singly bonded Cu atoms on the surface. For $\theta > 0.5$, the $[e]$ value becomes significantly larger, particularly at lower potentials, which suggests incipient metal crystalline formation at these coverages.

CH_4 adsorbs on Pt in the presence of Cu. In general, the charge to oxidize a combined ($\text{Cu} + \text{CH}_4$) layer is greater than that to oxidize either of the two separately produced layers, but far less than the sum of the charges to oxidize these two individual layers. Measurements of the $[e]$ value for the combined ($\text{Cu} + \text{CH}_4$) layer show that coverage with CH_4 species is unchanged in presence of Cu. This suggests that the Cu modifies the rates of formation and oxidation of the CH_4 layer in the same proportions. Studies of the effect of Cu on the over-all reaction of CH_4 to CO_2 show an inhibiting effect, which is the same over the whole

potential region of interest from 0.30 to 0.60v. The reaction mechanism changes in this potential region such that at the low potentials the rate limiting step is the oxidation of the adsorbed species (O-type), and at the high potentials it is the initial adsorption of CH_4 . Apparently, the Cu diminishes the rates of both of these reactions equally, but most likely by a simple area effect.

The adsorption of Ni from solutions containing Ni^{++} has been studied with smooth and platinized Pt electrodes. Even with very pure sources of Ni there appears to be some adsorption on the Pt. However, with an extensive adsorptive pre-electrolysis it has been shown that Ni does not adsorb appreciably on smooth Pt in the potential region of interest and that the bulk of the adsorption observed is due to minor impurities in the originally very pure Ni. On platinized Pt a minor oxidation wave corresponding to about $10 \mu\text{coul}/\text{r cm}^2$ ($< 5\%$ of a layer) is observed which may correspond to the oxidation of a small amount of adsorbed Ni. It has been observed that the minor impurity carried with Ni kinetically inhibits CH_4 adsorption.

Studies were made of the effect of Ni^{++} on the oxidation kinetics of CH_4 and on the oxidation kinetics of O-type CH_4 . O-type oxidation exhibits the following features: Initially, on the application of a current, the potential rises until the oxidation process starts. This potential varies with the applied current. After the removal of a small fraction of the adsorbed O-type the potential decreases, giving rise to an initial peak in the galvanostatic stripping curve. Subsequently a long plateau, where the potential scarcely changes with time, is observed until almost all of the O-type has been oxidized. At this time the potential starts to rise again.

Small concentrations of Ni^{++} in solution caused profound changes in the shape of the O-type stripping curve. At low currents the initial oxidation of O-type appears to begin more quickly in presence of Ni^{++} , but the potential at which most of the material is stripped is higher and the potential overshoot normally observed completely disappears. The main effect is thus one of inhibition. At high currents the preliminary

apparent enhancement of rate does not appear and some inhibition (at least 20 mv at fixed current) is observed over the whole stripping curve. With very high concentrations of Ni^{++} , e. g. 0.25 M, the behavior depends on how well the solution is pre-electrolyzed. Interestingly, it appears that the impurity carried with Ni^{++} (Co^{++} ?) enhances the oxidation of O-type, particularly at high current densities, and prevents what appears to be a minor adsorption of Ni.

The oxidation potentials are a linear function of the logarithm of the current density. For O-type formed in absence of Ni^{++} , the plateau potential-current relation has a slope of 116 mv/decade. The peak potential-current relation has a slope of 109 mv/decade suggesting that the process corresponds fairly closely to the transfer of 1 electron from O-type to the electrode. These potentials are shifted by the addition of Ni^{++} to the solution. Small concentrations of Ni^{++} (7 mM) merely shift the current-potential curve for the initial oxidation of O-type in the noble direction but do not appear to change the Tafel slope. A very concentrated Ni^{++} solution which has not been completely purified by pre-electrolysis causes a change in the Tafel slope with a greater inhibition of the process at low current densities but some enhancement of the process at very high current densities.

Ni^{++} in solution catalyzes the over-all CH_4 to CO_2 process. The extent of this catalysis varies with potential. At 0.30v, where O-type oxidation is rate limiting, no catalytic reaction is observed. At 0.40v the reaction rate is enhanced by about 50% for a Ni^{++} concentration of 0.10 mM. Above 1 mM Ni^{++} inhibits the over-all reaction at this potential. At 0.50v a 1 mM solution enhances the reaction by a factor of 2, but higher concentrations cause inhibition. The results appear to show that Ni^{++} enhances the rate of adsorption of CH_4 and hence its rate of oxidation.

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I. INTRODUCTION

In studies carried out previously, we have explored the mechanism of the anodic oxidation of the hydrocarbons CH_4 ^(1, 7), C_3H_8 ⁽¹⁻⁴⁾, and $n\text{-C}_6\text{H}_{14}$ ⁽⁵⁾ on Pt electrodes in hot (130°C) concentrated (80 wt %) H_3PO_4 . The following is a brief summary of our conclusions based on previous observations:

(1) The reaction must occur by means of adsorption, and all intermediates between the hydrocarbon reactant and the product (CO_2) are adsorbed on the electrode.

(2) When hydrocarbons adsorb on Pt electrodes, three adsorbed species are found. These are the $\text{CH-}\alpha$, $\text{CH-}\beta$ and O-type residues.

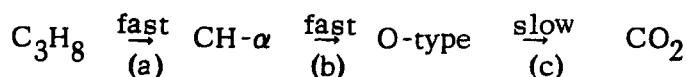
(3) The $\text{CH-}\alpha$ material can be hydrogenated. It is therefore assumed to be an alkyl group or a partially hydrogenated alkyl group. Gas chromatographic analysis of the effluent after hydrogenation of the $\text{CH-}\alpha$ material shows that some C-C bond breaking has occurred⁽¹²⁾. The amount of $\text{CH-}\alpha$ increases with increasing molecular weight of the hydrocarbon. Thus, there is no $\text{CH-}\alpha$ with CH_4 , but it contributes about half of the charge for the adsorbate of $n\text{-C}_6\text{H}_{14}$ ⁽⁵⁾. In the case of C_3H_8 , a composition of somewhere between >C and >CH has been suggested to correspond to the $\text{CH-}\alpha$ material at low potentials⁽¹⁾.

(4) The $\text{CH-}\beta$ material is not cathodically desorbable by hydrogenation. It is unreactive towards oxidation and its amount increases from CH_4 to $n\text{-C}_6\text{H}_{14}$. Its oxidation state is such as to suggest that most of the original CH bonds of the hydrocarbon have not been replaced by CO bonds: it may be a carbonaceous polymer.

(5) The major constituent of the adsorbed layer in terms of coverage is O-type. O-type is found for all hydrocarbons thus far investigated and appears identical⁽⁶⁾ with the species reported

by Giner^(8, 9) "reduced CO₂." Its oxidation state and the fact that it cannot be hydrogenated, suggest that it contains oxygen. Based on results with CH₄⁽¹⁾, a composition \approx C(OH) was suggested.

(6) We have shown that the oxidation of O-type to CO₂ is the rate limiting step at low potentials (certainly for potentials \leq 0.35 v vs. RHE) for the oxidation of CH₄⁽¹⁾ and C₃H₈^(1, 10) and probably for a range of higher hydrocarbons. The over-all scheme we have suggested for C₃H₈⁽¹⁾ is



The oxidation of O-type probably occurs by participation of H₂O molecules adsorbed on bare sites on the electrode and we have shown that the presence of CH- α on these sites inhibits O-type oxidation^(1, 10); similarly, lowering the water concentration in the solvent inhibits the reaction.

(7) At higher potentials (e.g. 0.5 v) the above mechanism does not operate. The slow step becomes the initial adsorption process itself and the adsorbate reacts to form CO₂. The reaction probably does not proceed via O-type in this case, however.

A number of important aspects of the reaction mechanism remain to be resolved: e.g. (a) the quantitative definition of the role of water in the oxidation of O-type and a decision as to whether the reacting H₂O has to be adsorbed on the electrode, and (b) the chemical structure of the important CH- α species. Since it appears that CH- α oxidation becomes rate limiting with higher molecular weight hydrocarbons, this would become more important with those compounds.

It is clear that there is much more about the reaction which we need to know for a complete understanding of its mechanism. However, our understanding of the reaction is now at a sufficiently advanced stage that we can begin to see how to use

our knowledge in catalyst development. The most important immediate requirement in hydrocarbon fuel cell technology is to find some way to break away from noble metal catalysts which are expensive and rare. Correspondingly, the emphasis in our program has moved towards using our understanding of the mechanism of hydrocarbon oxidation as a guide in catalyst development.

Our approach to the possible development of non-noble metal hydrocarbon fuel cell catalysts is via adsorption and was described in our last report. The essence of the method is that in sub-monolayer amounts the reversible potential for metal dissolution is shifted in the noble direction. Therefore, the stability of the non-noble metal against corrosion is enhanced.

In our last report, exploratory measurements for the adsorption of Cu on Pt were reported. It was shown that Cu does adsorb at potentials anodic to that corresponding to the Cu^{++}/Cu reaction and that this Cu layer inhibited the rate of the over-all oxidation of CH_4 to CO_2 by slowing down the rate limiting step, which is the oxidation of the O-type intermediate to CO_2 . There were, however, some anomalies in the behavior of the adsorbed Cu layer, and these have been resolved by further experimentation. In addition, a study has been made of the effect of Ni^{++} on the adsorption and oxidation of CH_4 . Particularly interesting is the observation that addition of Ni^{++} to the solution enhances the over-all oxidation rate of CH_4 by about a factor of 2 despite the fact that little or no Ni adsorption is observed.

As before, experiments were carried out with Pt electrodes at 130°C in 80% H_3PO_4 . Details of the experimental procedures have been reported previously⁽¹⁻⁷⁾.

II. Cu ADSORPTION ON Pt

Further studies of Cu adsorption on Pt at 130°C have been made. Cu adsorption on Pt is a diffusion controlled process, as evidenced by the large effect of stirring. This stirring effect is illustrated in Fig. 1 for platinized Pt where adsorption was allowed to occur at 0.30v. After two minutes there is about a four-fold increase in adsorption as the result of stirring. After three minutes, the rate of adsorption is slower than a diffusionally controlled process. Most of our subsequent experiments were carried out with stirring at 130°C.

Figure 2 shows Cu adsorption with stirring on a smooth platinum electrode as a function of time at 0.30v. At the low Cu^{++} solution concentrations, 3 and 7 μM , the adsorption increases linearly with time for the first five minutes. At 30 μM it only increases linearly for approximately the first minute. Further, the increased adsorption is not directly proportional to the concentration. At 3 μM after 30 seconds there is a 12 $\mu\text{coul/r cm}^2$ adsorbed, whereas the 30 μM there are 60 $\mu\text{coul/r cm}^2$, which is only a five-fold increase for a ten-fold increase in concentration. Steady state is achieved in about ten minutes.

The charge to oxidize the steady state copper layer is shown in Fig. 3 as a function of concentration and potential of adsorption. The maximum is seen around 0.20v vs. the reversible hydrogen electrode with a slow descent to 0.60v. Cu adsorption is then found over a potential range which is about 0.1v wider than with the hydrocarbons, but the general shape of the curve is very similar. The effect of concentration is most marked in the range 0.10 - 0.35v. Between 3 and 7 $\mu\text{M Cu}^{++}$, there is very little difference in the amount of charge measured at each potential in the range 0.40 - 0.60v. The effect of concentration is more marked at 30 μM but again the charge increment with concentration decreases as the potential of adsorption is increased.

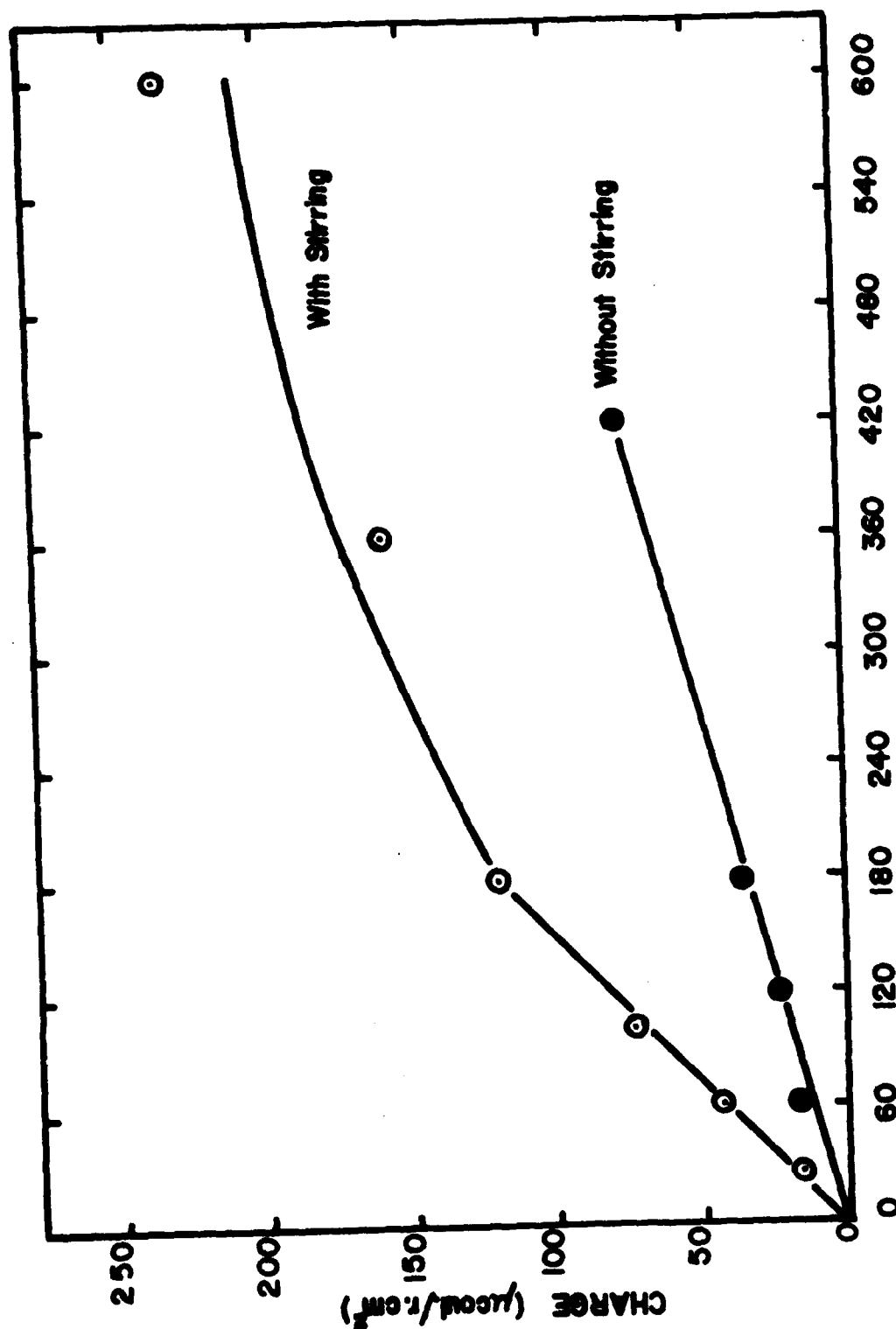


Fig. 1 Effect of stirring at 0.30v on the rate of Cu^{++} adsorption on platinized platinum.

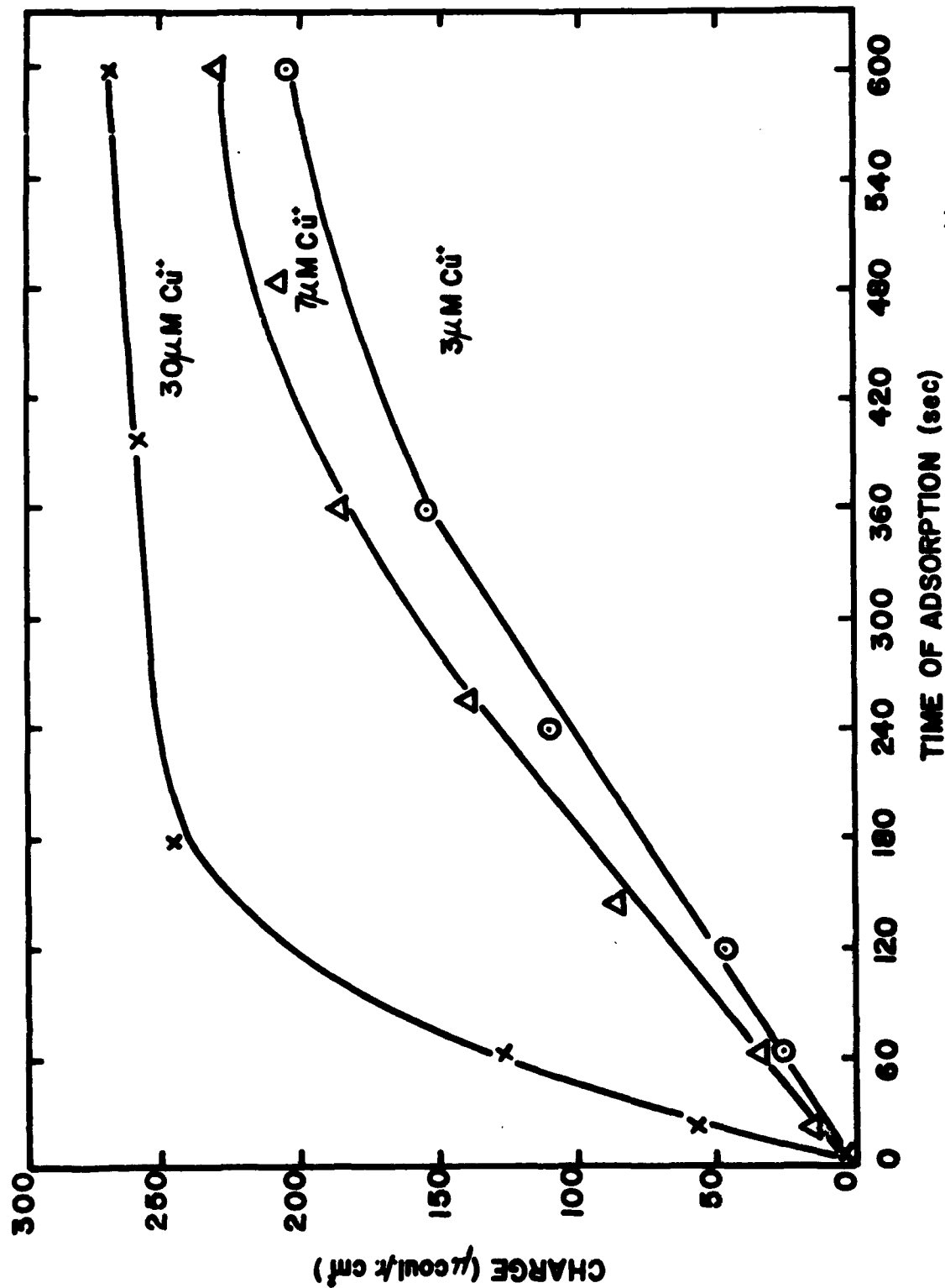


Fig. 2 Rate of charge accumulation as a function of time of adsorption and Cu^{++} concentration in solution.

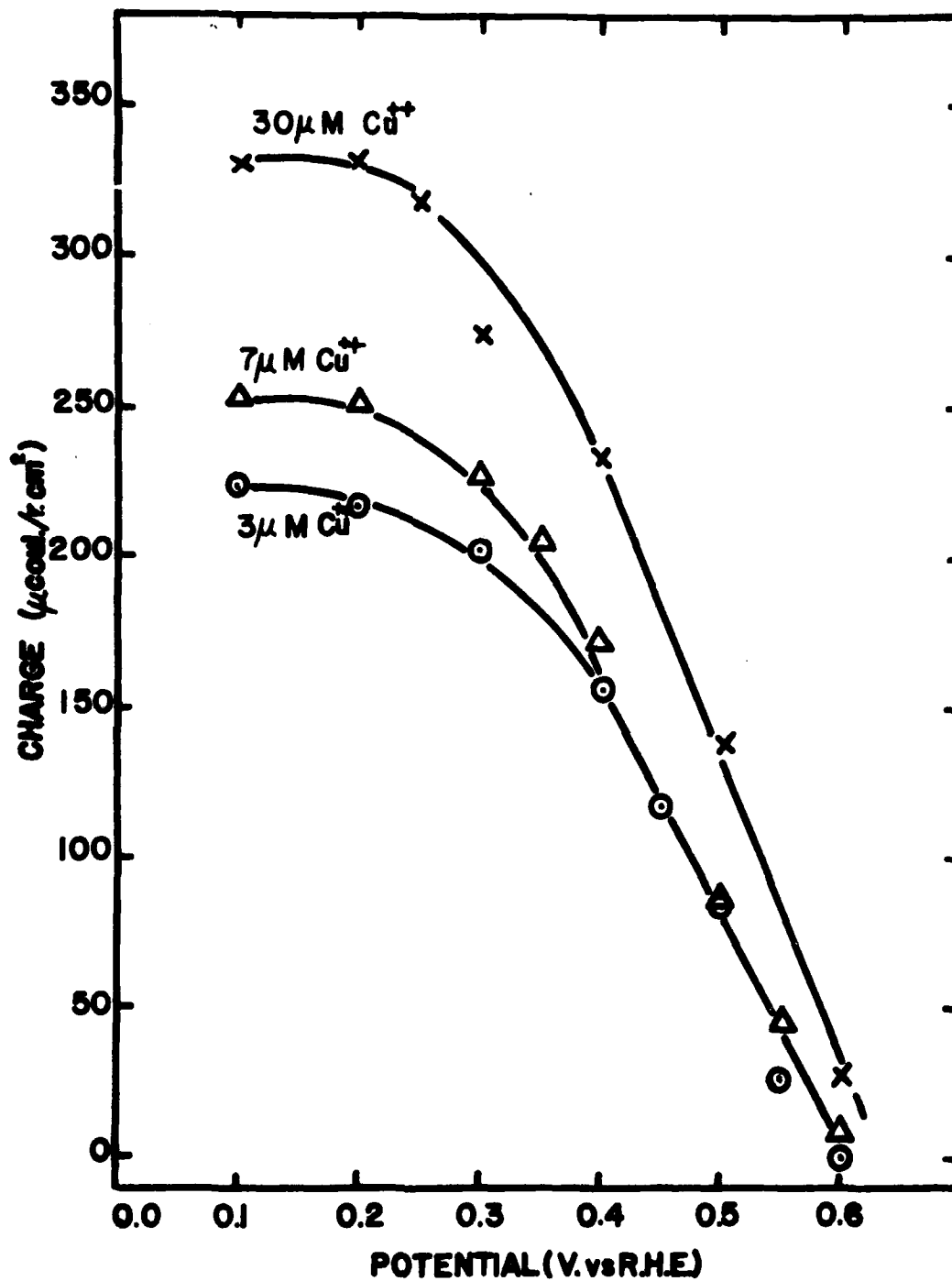


Fig. 3 Steady state adsorbate charge on smooth Pt as a function of potential of adsorption and Cu^{++} concentration in solution.

Figure 4 illustrates the amount of charge passed in oxidizing the adsorbed Cu layer as the concentration and potential are raised on platinized platinum. The adsorption in this case is greatly increased by addition of more Cu^{++} to the electrolyte. In addition, the general shape of the Q-E curve is altered with no potential region of invariant coverage. At $30 \mu\text{M Cu}^{++}$, there is a decrease of $\sim 50 \mu\text{coul}$ for every 0.1v increase in adsorption potential up to 0.50v . At the low concentration, on the other hand, the biggest change in coverage is between 0.20 and 0.30v , with a decrease of $\sim 30 \mu\text{coul/r cm}^2$ between the other 0.1v steps.

On smooth Pt, we can interrupt this adsorption process at regular intervals and measure and compare the Cu coverage and the charge to oxidize the adsorbed Cu layer. This relationship gives us the number of electrons per site, $[e]$, which are involved in the oxidation process. Figure 5 exhibits the ratio of the coverage and charge accumulated with stirring as a function of potential of adsorption. The first half of the electrode is covered with the same material irrespective of the adsorption potential. This species releases 1.8 electrons per site on oxidation and corresponds closely to the two electrons one would expect if oxidizing the adsorbed copper metal back to the ion, i. e. $\text{Cu}^0 \rightarrow \text{Cu}^{++} + 2\text{e}^-$. It probably actually represents a mixture of singly (the major component) and doubly bonded Cu atoms (two electrons and one electron/site, respectively).

At coverages greater than 0.5 , the relationship between charge and coverage depends on the adsorption potential. At 0.20v the slope is just about four, indicating that the Cu is probably plating on top of itself and one would find two copper atoms attached to each platinum site. At 0.30v and 0.40v the material corresponding to the higher coverages only releases three electrons per site. This probably implies that equal numbers of the Pt atoms are covered with two atoms of Cu ($[e] = 4$) and with a simple Cu atom ($[e] = 2$). The variation towards higher $[e]$ at lower potential is expected, because of the increasing tendency to form metallic Cu. Presumably, the adsorbed layers with higher $[e]$ are the precursors of such metal formation.

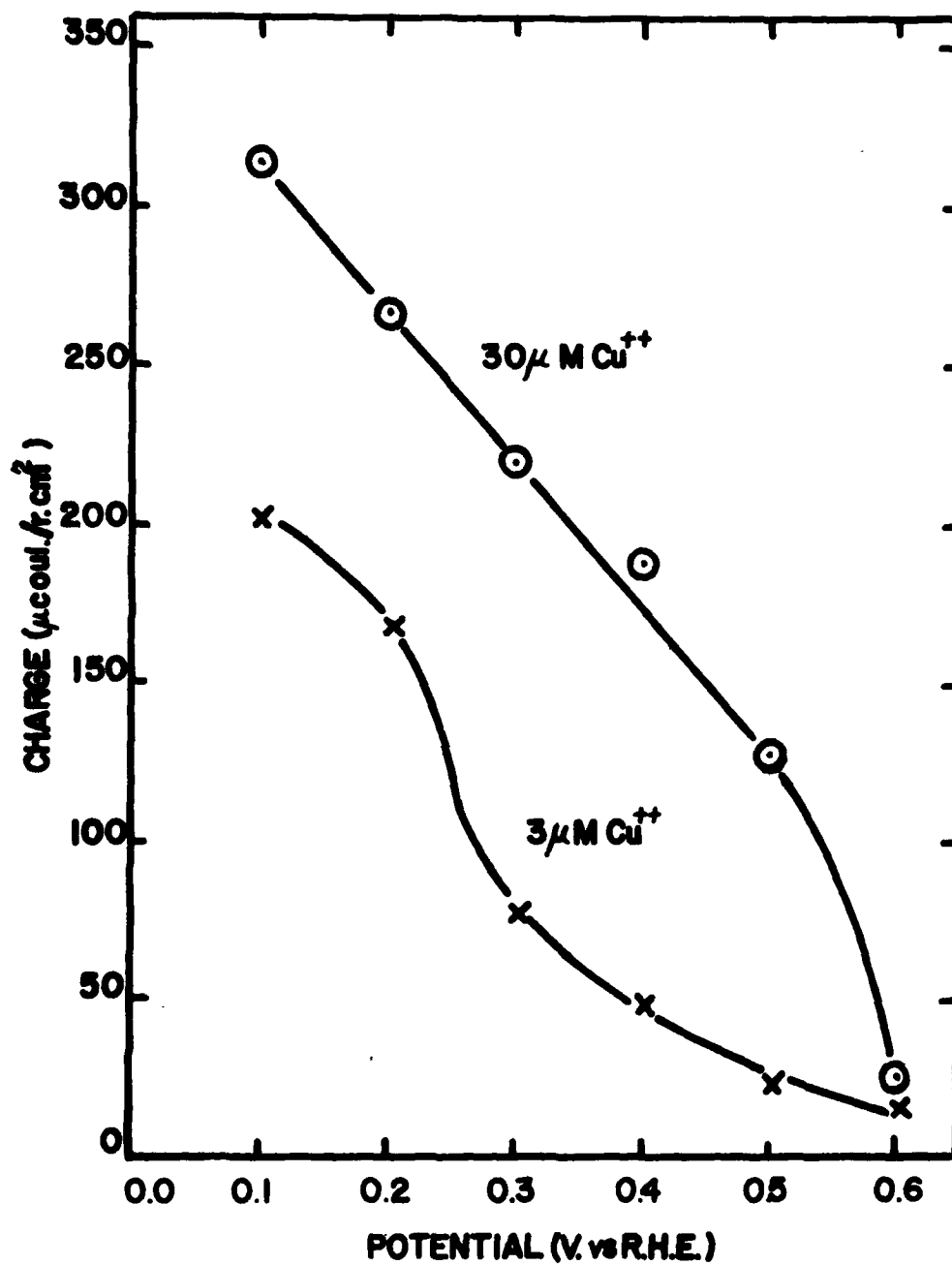


Fig. 4 Steady state adsorbate charge on platinized Pt as a function of potential of adsorption and Cu^{++} concentration in solution.

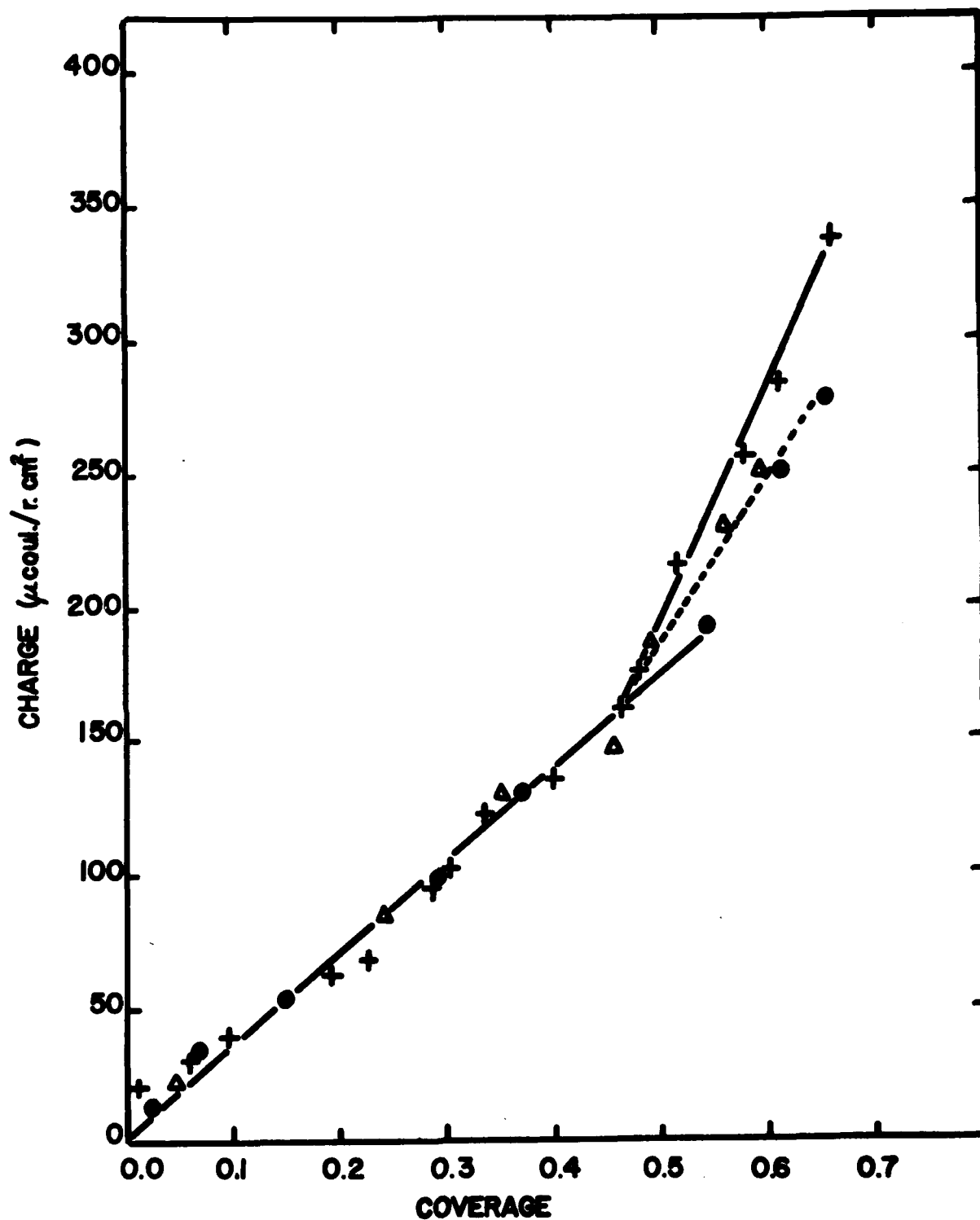


Fig. 5 Ratio of charge accumulation to Cu coverage as a function of potential during adsorption (+, 0.20v; •, 0.30v; Δ, 0.40v).

Previously, we had found that the major $[e]$ value for Cu is ~ 1.2 electrons/site. The difference between these values and the present results appears to relate to the rate of adsorption. Previously the solutions were not stirred, whereas gas stirring was used here. It would appear that the mode of adsorption is a function of the adsorption rate. It is not at all clear why this should be the case. What is important, however, is that $[e]$ for O-type CH_4 is ~ 1.2 , and thus the organic species can easily be distinguished from the Cu.

III. CO-ADSORPTION OF Cu AND CH₄

Comparing the steady state charge for oxidation of the adsorbed species as a function of potential of adsorption (Fig. 6), we find that the ($30 \mu\text{M Cu}^{++} + \text{CH}_4$) is essentially the same as that for this concentration of Cu^{++} alone. This would indicate that the adsorbate is probably mostly Cu. However, the ($3 \mu\text{M Cu}^{++} + \text{CH}_4$) does show an increase over that which is observed with Cu^{++} alone. This charge is less than the sum of the individual adsorbates (from solutions containing only Cu^{++} and CH_4 respectively), but it is evident either that the Cu promotes CH_4 adsorption and/or that both species are adsorbed. Similar to the effect of Cu^{++} concentration, the enhancement in Q is greatest in the potential range from 0.10 to 0.30v and declines with increasing potential.

Figure 7 shows the steady state adsorbate as a function of potential of adsorption and concentration on platinized platinum. The effect of co-adsorption is most marked in the potential range 0.30 - 0.50v. Again, however, the charge to oxidize the combined ($\text{Cu} + \text{CH}_4$) adsorbed layer is much smaller than the sum of the two measured separately.

It would be of particular interest to examine the ratio of the coverage and charge on the platinized platinum since the enhancement is in the potential region in which we are most interested with respect to the hydrocarbon anode. The technique which we employ to determine coverage involves hydrogen charging. This cannot be done on platinized platinum, however. In Fig. 8 we show a comparison of the CH_4 , Cu and ($\text{Cu}^{++} + \text{CH}_4$) adsorbates on smooth Pt. Although the charge to oxidize the adsorbed layer in presence of Cu^{++} is higher than for pure CH_4 , it is evident that the amount of CH_4 is essentially unchanged and that the increase is due to Cu adsorption. This implies that adsorbed Cu does not significantly affect the relative rates of the reactions to form and to oxidize the adsorbed CH_4 layer.

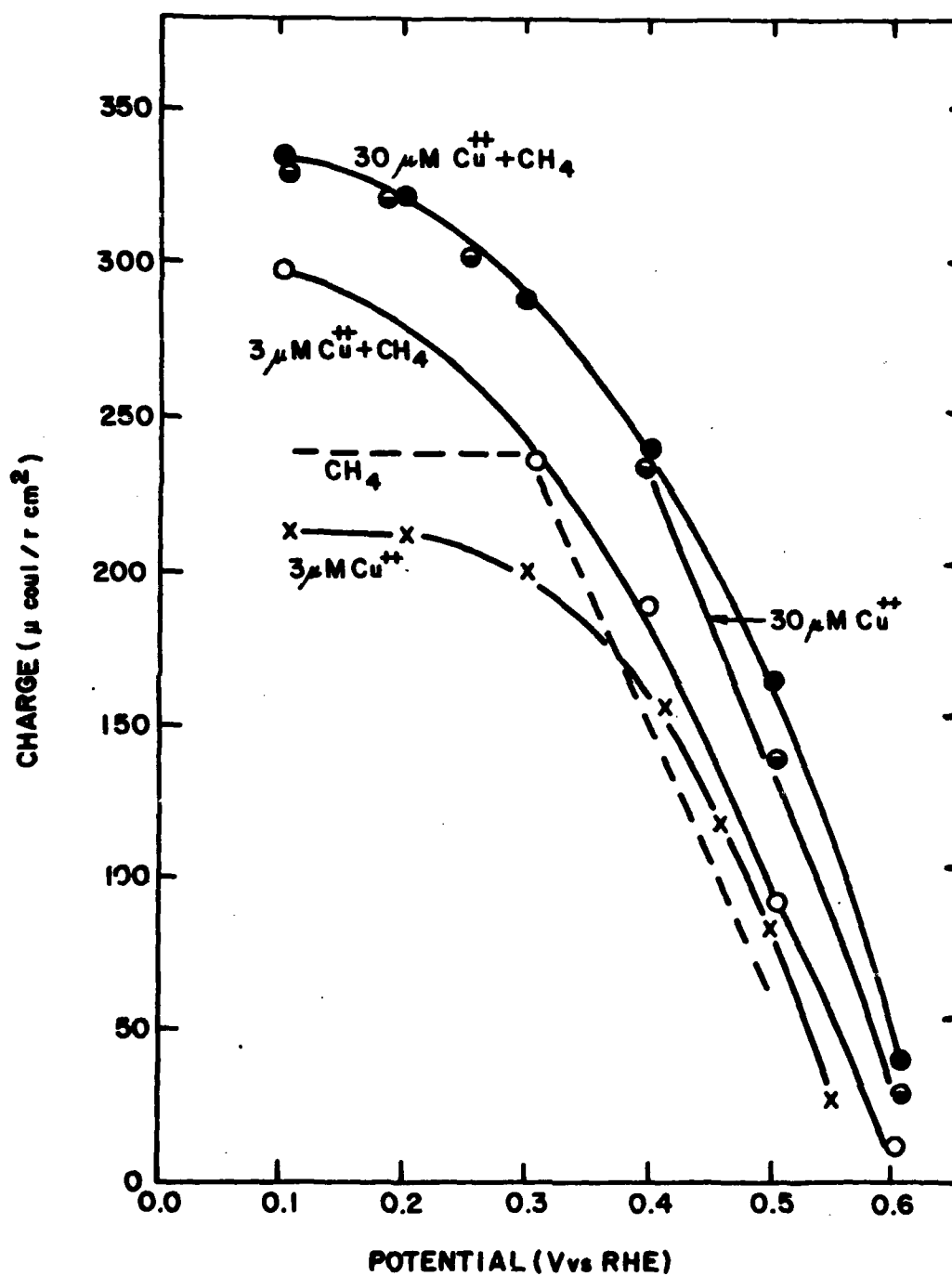


Fig. 6 Effect on smooth platinum of Cu $^{++}$ concentration on CH $_4$ steady state adsorbate charge as a function of adsorption potential.

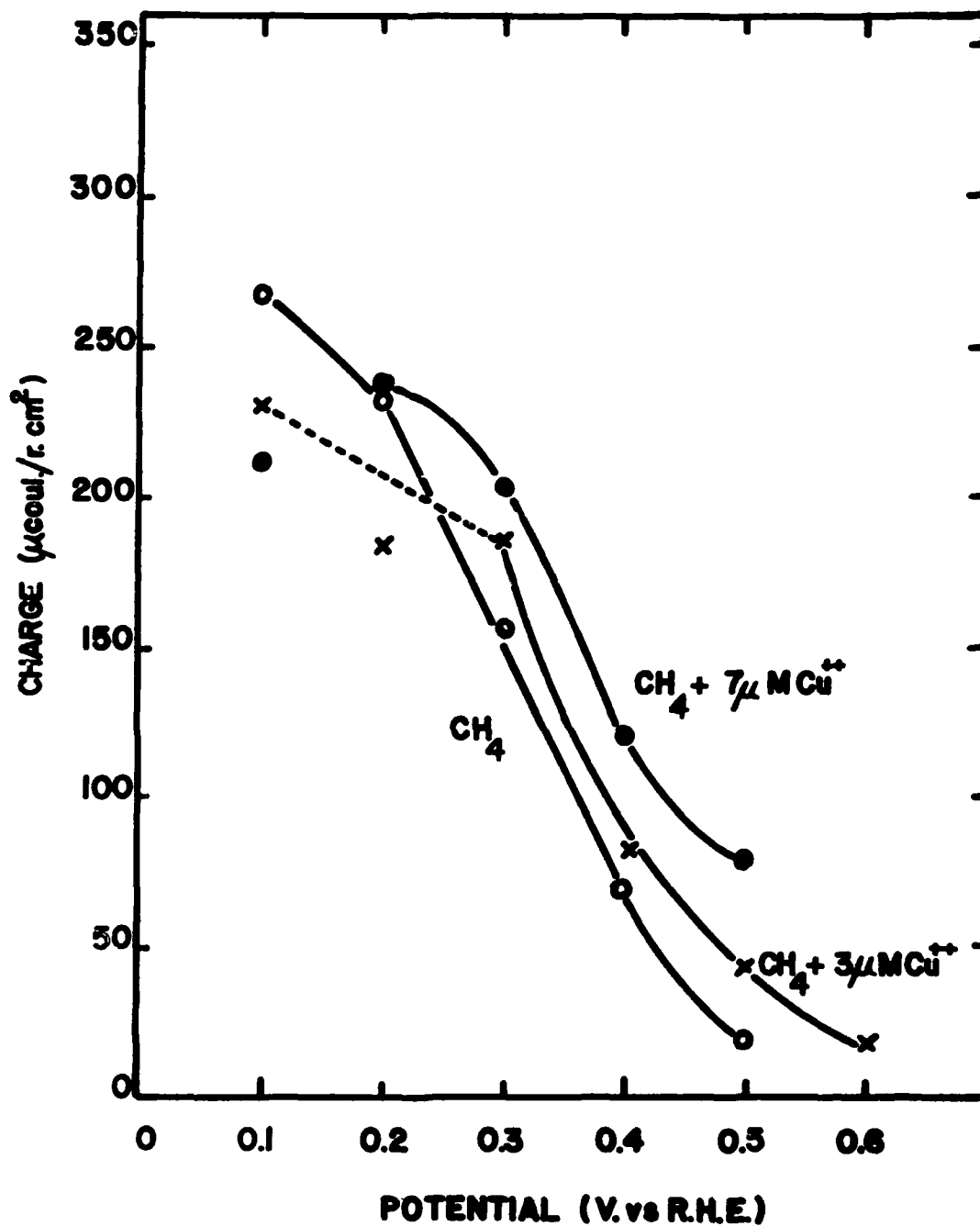


Fig. 7 Effect on platinized platinum of Cu⁺⁺ concentration on CH₄ steady state adsorbate charge as a function of adsorption potential.

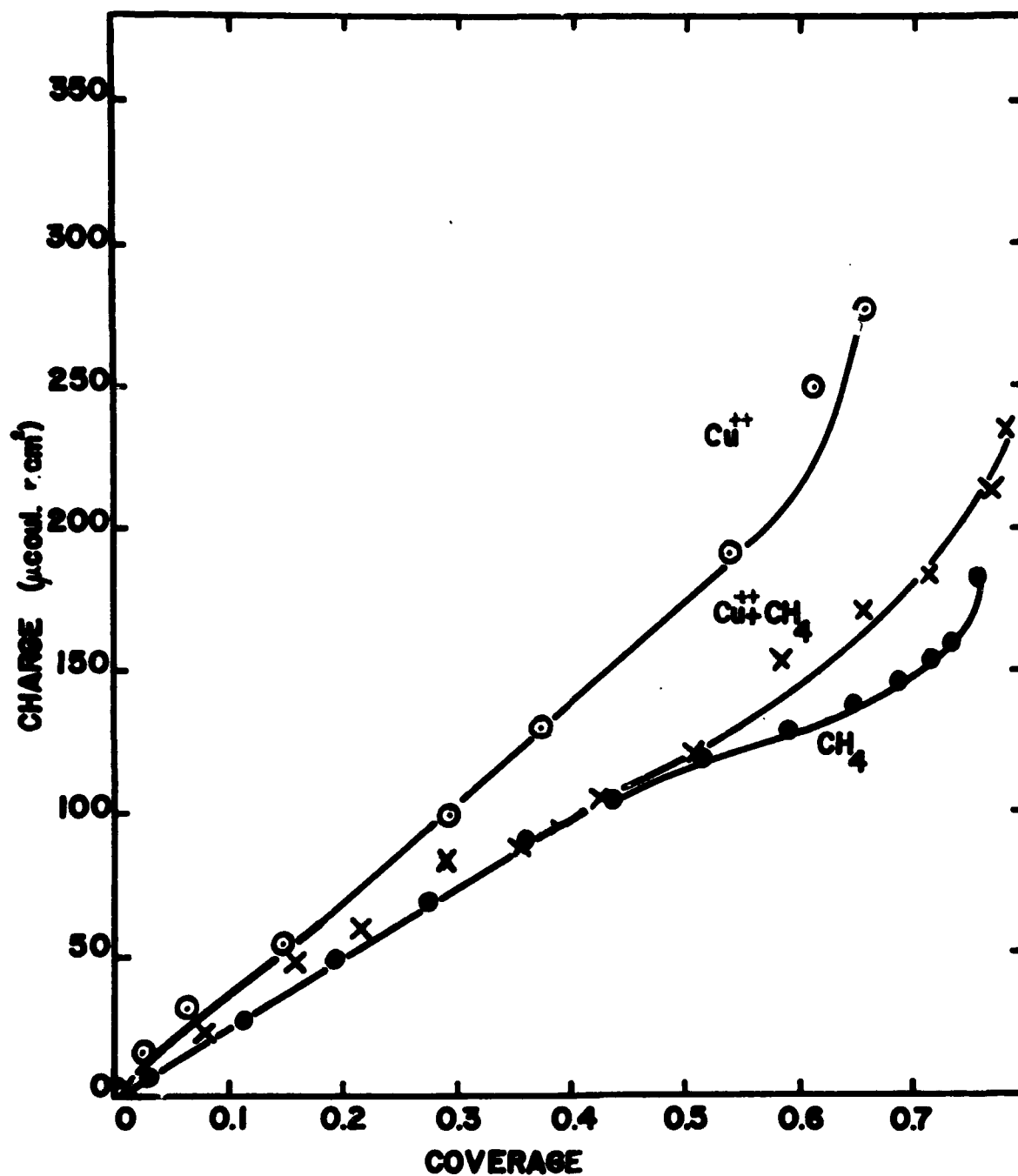


Fig. 8 Comparison of ratios of adsorbate charge to coverage during adsorption of Cu , CH_4 , and $(\text{Cu}^{++} + \text{CH}_4)$.

The absolute rates of these reactions are diminished, however, as shown by results on platinized Pt. Although we cannot use platinized Pt to measure coverages, we can use it to measure currents for the over-all reaction. Figure 9 shows the CH_4 oxidation current as a function of Cu^{++} concentration, and as reported previously, we see that the addition of Cu^{++} acts as an inhibitor for the over-all oxidation rate. This is true at all potentials, with the poisoning increasing uniformly as more Cu^{++} is added to the system.

It is interesting that this inhibition is about the same at 0.60v, where the rate limiting step is the initial adsorption, as it is at 0.30v, where O-type oxidation is rate limiting. Again, this result implies that Cu (and/or Cu^{++}) inhibits both the initial adsorption and the adsorbate oxidation reactions equally.

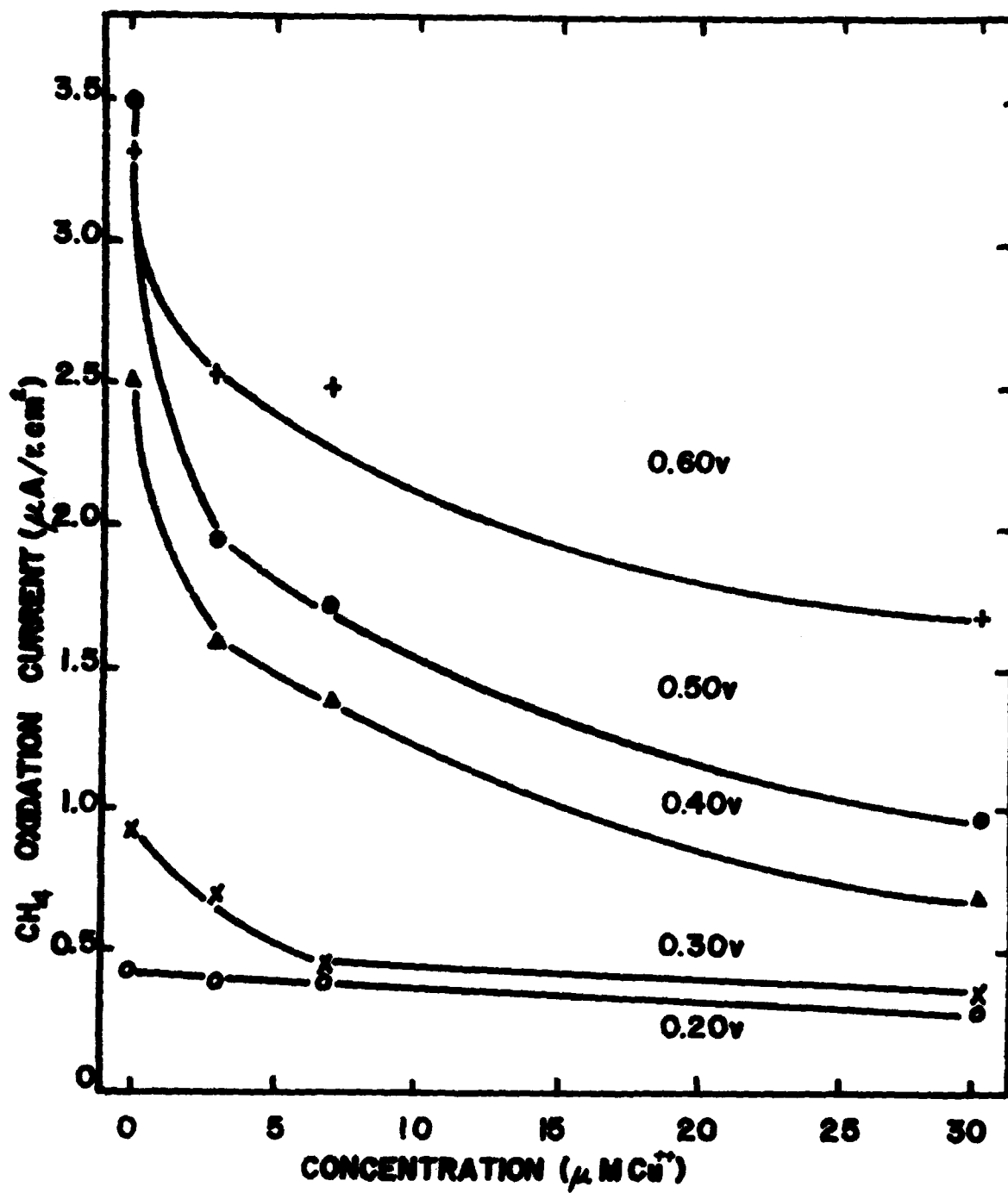


Fig. 9 CH₄ oxidation current as a function of Cu²⁺ concentration and potential of adsorption.

IV. NI ADSORPTION ON Pt

Nickel is a useful catalyst for carbon-hydrogen and carbon-carbon bond-breaking reactions⁽¹¹⁾ and its use as an adsorbed catalyst for hydrogen oxidation is therefore of some interest.

Our original investigations with Ni involved dissolving either carbonyl Ni or a known weight of five nine's Ni rod in phosphoric acid. We had a great deal of difficulty in dissolving the nickel. It took several hours to obtain 20 ml of 10^{-3} M solution and it seemed impossible to achieve concentrations greater than 10^{-1} M. We were hoping to avoid the introduction of other metals, e. g. Co and Cu which would be present in trace amounts if we used a Ni compound.

The technique which we employed was to set up the system with 90% H_3PO_4 and 15% volume/volume of 30% H_2O_2 . After three hours with vigorous N_2 stirring and the disappearance of any gas evolution, a fuel cell electrode was inserted into the solution and held at 0.30v for 24 hours to allow the removal of any adsorbable impurities. After removal of the fuel cell electrode there was no adsorption on a smooth Pt electrode at 0.3v with gas stirring of the solution for 20 minutes. The Ni solution was then added with confidence that any adsorption would be due to the introduction of the Ni solution.

Once we had observed that there appears to be adsorption of Ni, we established that the charge to oxidize this adsorbate is independent of the current density used to make the measurement. In the range 5 ma to 110 ma/ r cm^2 the adsorbate charges were identical.

The initial experiments with Ni were somewhat confusing. Figure 10 shows the charge to oxidize the adsorbed layer. Initially it increases linearly with $\tau^{1/2}$, but it is independent of concentration. Yet, as shown in Fig. 11, the charge formed at 0.20v was increased by stirring. If we were introducing an impurity with the Ni, its concentration should have increased proportionally to the Ni^{++} concentration and the adsorption kinetics in quiescent solution should have varied with concentration of added Ni^{++} . We felt then that the adsorbate had to be Ni adsorbed on the electrode.

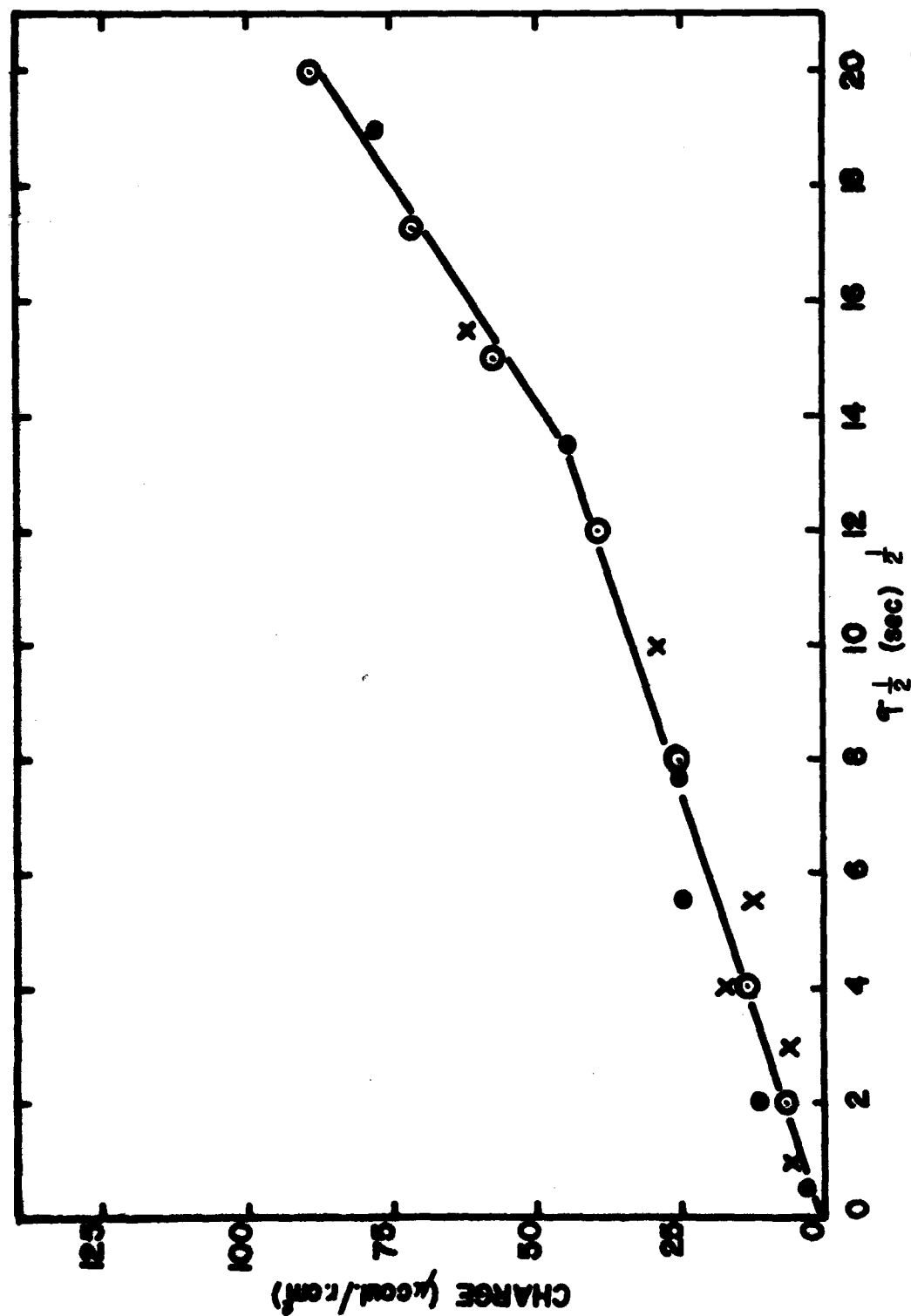


Fig. 10 Rate of charge accumulation without stirring as a function of time of adsorption at 0.2v and Ni^{++} concentration in solution (\bullet , $2 \times 10^{-4} \text{M Ni}^{++}$; \circ , $1 \times 10^{-3} \text{M Ni}^{++}$; \times , $1.5 \times 10^{-2} \text{M Ni}^{++}$).

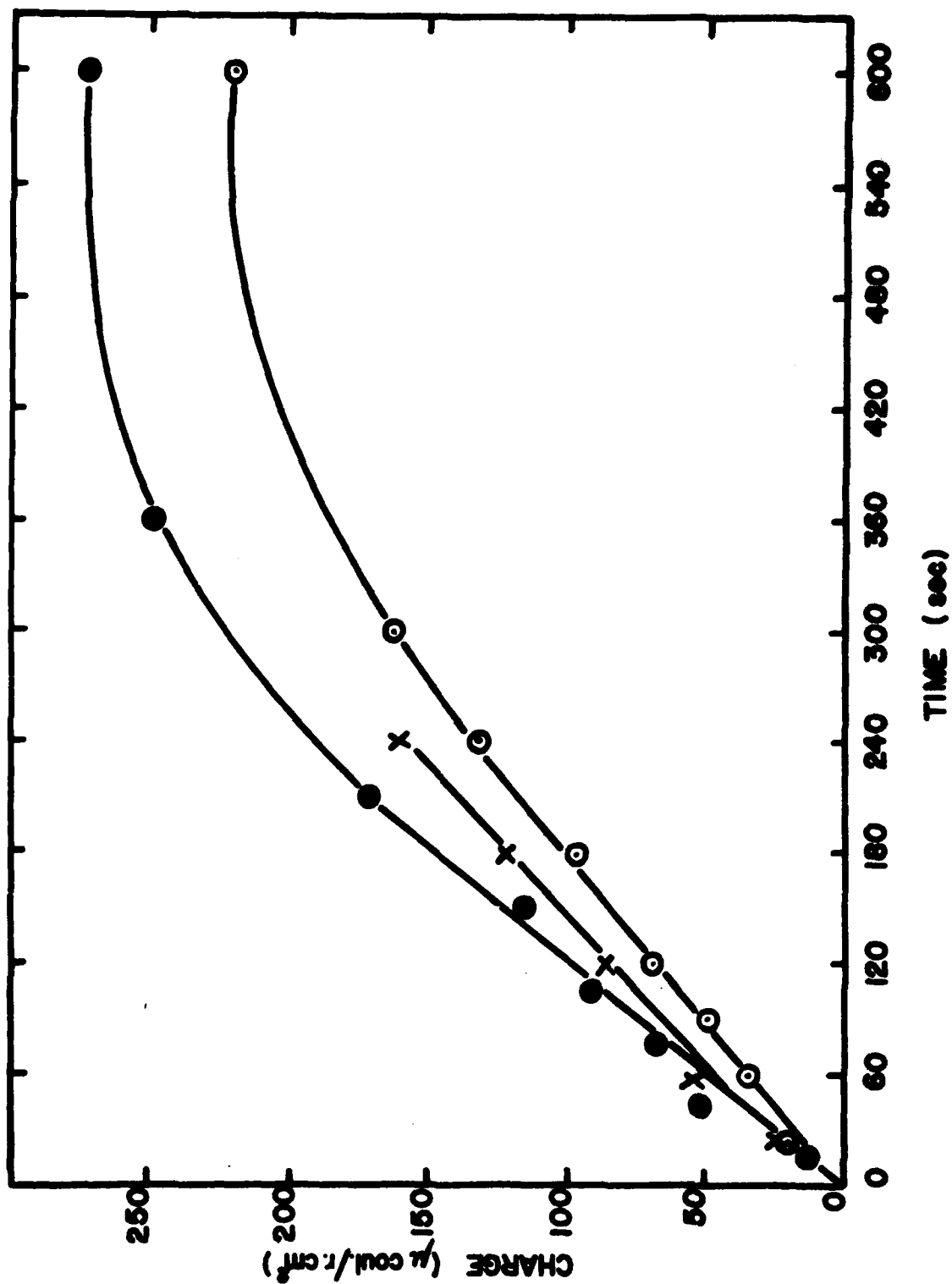


Fig. 11 Rate of charge accumulation with stirring as a function of time of adsorption at 0.2v and Ni^{++} concentration in solution (\odot , $2 \times 10^{-4} \text{ M Ni}^{++}$; \times , $1 \times 10^{-3} \text{ M Ni}^{++}$; \bullet , $1.5 \times 10^{-2} \text{ M Ni}^{++}$).

The steady state adsorbate formed using the carbonyl Ni (International Nickel No. 287) is shown in Fig. 12 (open figures and lower concentrations) and the higher concentrations (dark figures) were obtained by dissolving Ni rod. It is evident that there is more "Ni" adsorption as we increase the concentration of Ni^{++} . If for a given amount of oxidizable charge we plot the potential at which this occurs as a function of the log of the Ni^{++} concentration, we can calculate the number of electrons released on oxidation of the adsorbate. We would expect a linear relationship for the lower concentration, with a slope of about 40 mv for 1 electron and 80 mv for 2 electrons. Figure 13 illustrates that we do not have a linear relationship, and it is difficult to draw any conclusion about the number of electrons involved in the reaction process.

Because of the difficulty in obtaining readily accessible high Ni^{++} concentration in solution by dissolving Ni metal, further studies were made using NiCO_3 (Baker Analyzed) dissolved in H_3PO_4 . This salt contains 0.08% Co and 0.003% Cu which might interfere with our measurements. Such material was eliminated after addition to the main solution by adsorption on a high surface area fuel cell electrode. After 24 hours with the fuel cell electrode in solution, there was no adsorption with Ni^{++} . There was Ni^{++} present in the solution and its concentration (up to 0.2M) was verified by using a colorimeter. The initial "Ni" adsorption must have arisen from an impurity, therefore.

Analysis of CH_4 adsorption data in presence of Ni^{++} shows that when the solution has been previously adsorptively pre-electrolyzed, there is no increased adsorption over a pure CH_4 saturated solution. Further, at the high current densities used in such measurements, i. e. greater than 60 ma/r cm^2 , there is no change in the character of the stripping chronopotentiograms.

We conclude from these results then that there is no appreciable Ni adsorption on Pt. Data in the next section will indicate a small amount of adsorption ($\sim 10 \mu\text{coul/r cm}^2$ at 0.30v) on platinized Pt and a gross effect on the oxidation of O-type CH_4 , however.

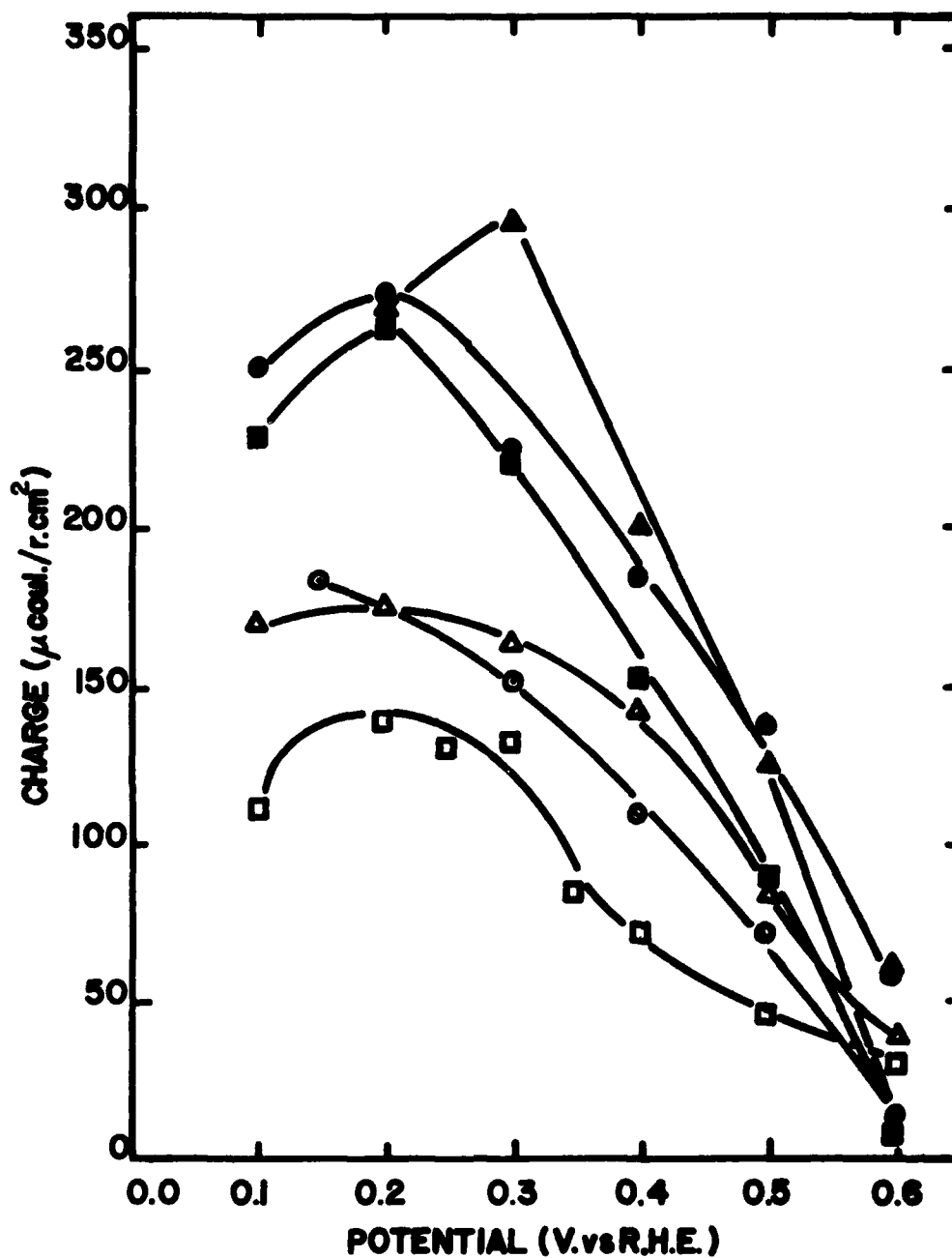


Fig. 12 Steady state adsorbate charge on smooth platinum as a function of potential of adsorption and concentration of Ni^{++} in solution.
 (□, $2 \times 10^{-6} \text{M Ni}^{++}$; ◊, $6 \times 10^{-6} \text{M Ni}^{++}$; Δ, $3 \times 10^{-5} \text{M Ni}^{++}$;
 ■, $1 \times 10^{-4} \text{M Ni}^{++}$; ●, $1 \times 10^{-3} \text{M Ni}^{++}$; ▲, $1 \times 10^{-2} \text{M Ni}^{++}$;

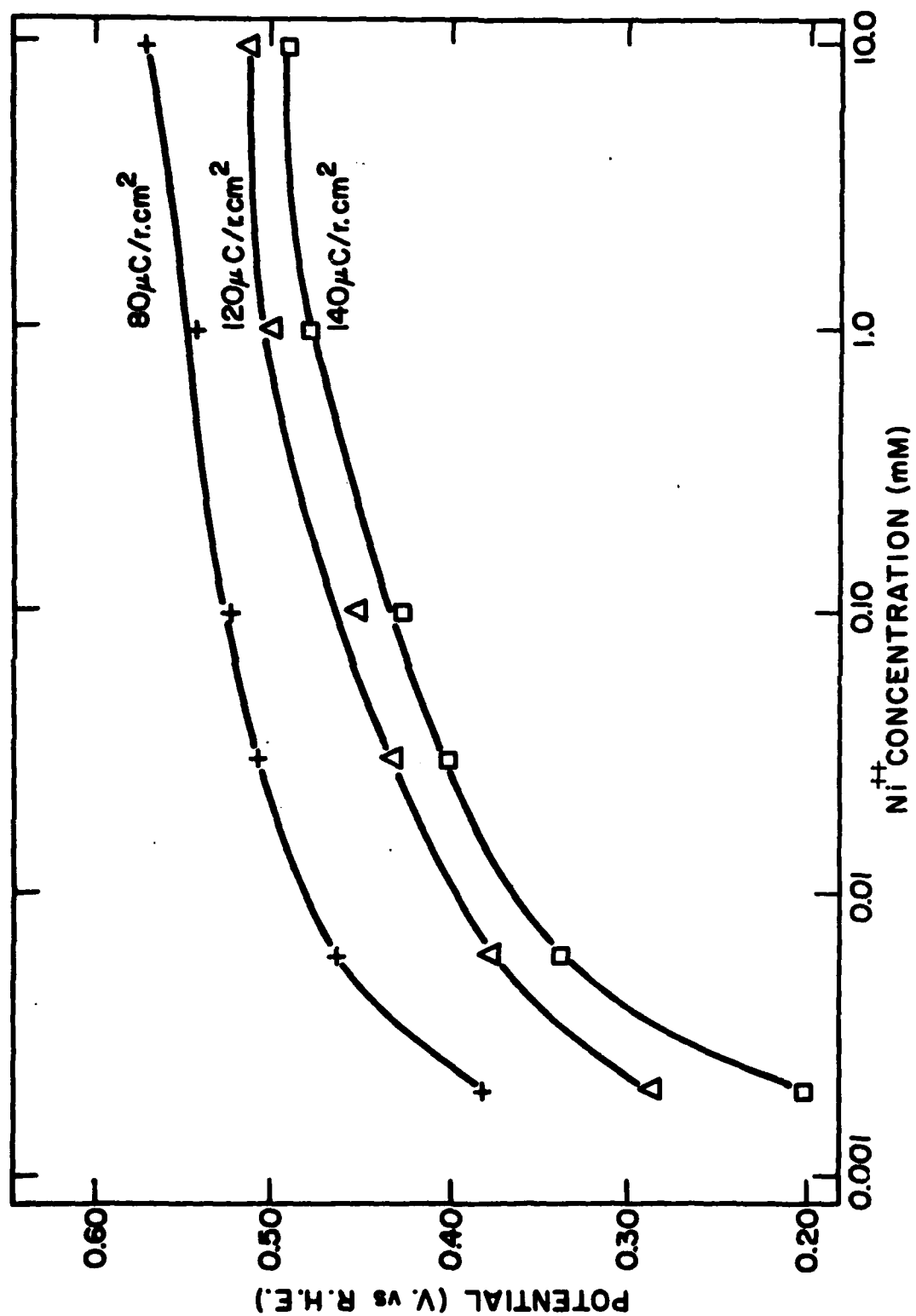
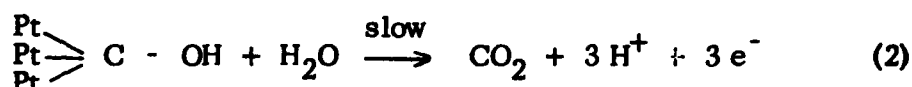
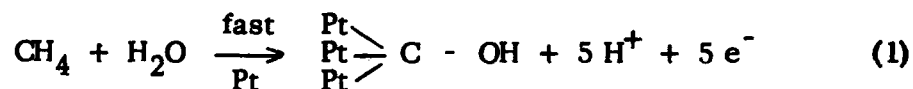


Fig. 13 Potential - Ni⁺⁺ concentration relation for constant amounts of "Ni."

V. EFFECT OF Ni^{++} ON THE OXIDATION KINETICS OF CH_4 AND O-TYPE CH_4

The mechanism which we believe is valid for the over-all oxidation of CH_4 at low potentials ($\leq 0.35\text{v}$) is⁽¹⁻⁷⁾:



Here, the rate-limiting step is reaction (2) and the species $\begin{array}{c} \text{Pt} \\ \text{Pt} \diagup \\ \text{Pt} \diagdown \end{array} \text{C} - \text{OH}$ we have called "O-type."

At higher potentials, we believe that the initial adsorption of CH_4 is rate-limiting for the over-all reaction, viz.



Here, we believe that the results on the whole tend to rule out that the reaction can proceed via O-type.

The aim of our catalyst development program is not only to seek adsorbed layers that will enhance the over-all reaction directly, but also to look for possibilities to develop polyfunctional catalysts. Thus, we examine each adsorbed layer for its catalytic activity for reactions (2) and (3) as well as for the over-all reaction.

Initial experiments were designed to examine the effect of Ni^{++} on O-type oxidation. Having achieved a cleaner system than in previous experiments, due to the use of a removable pre-electrolysis fuel cell electrode, we re-examined the oxidation of the O-type material in the

absence of Ni^{++} . The experiments were carried out as follows: The adsorbed layer was formed at 0.30v for ten minutes with stirring and one minute without, to establish the steady state and a quiescent solution. The potential was lowered to 0.20v where desorption of the adsorbate is not likely to occur because the oxidation rate of O-type is low at this potential. N_2 was bubbled through the solution through a different water presaturator, to the cell in order to remove CH_4 from the electrolyte and prevent readsorption during the stripping of O-type. After ten minutes, the N_2 was shut off and the potential was subsequently raised to 0.30v for one minute in a quiescent solution. Then the small galvanostatic pulse to oxidize O-type was applied.

Figure 14 shows the initial regions for the low current density stripping of O-type CH_4 . We see an initial overshoot, particularly well defined at low current densities. This is followed by a well defined plateau, where most of the oxidation of O-type material occurs. The potential at which this stripping takes place increases as the current density increases. The general shape of the curve is very similar over two orders of magnitude in current.

The oxidation potentials are a linear function of the logarithm of the stripping current density (Fig. 15). The plateau potential-current relation has a slope of 116 mv per decade and extrapolates back to $0.19 \mu\text{a/r cm}^2$ at 0.30v. The potential of the overshoot (the peak) shows a tafel slope of 109 mv/decade and the line extrapolates to $\sim 0.15 \mu\text{a/r cm}^2$. The tafel slope for the peak potential suggests that the rate-limiting process here is the removal of a single electron from O-type.

Figures 16, 17 and 18 demonstrate the considerable effect that 7 mM Ni^{++} has on the general shape of the O-type stripping curve. It must be pointed out again that with this Ni^{++} concentration there is no Ni adsorption with N_2 stirring. Also, the stripping curves with the steady state CH_4 coverage (measured with $60 \mu\text{a/r cm}^2$) show no change in shape or charge compared with a Ni^{++} free electrolyte. At $0.5 \mu\text{a/r cm}^2$ (Fig. 16) the initial oxidation appears to begin more quickly but the potential at which most of the material comes off is higher and the

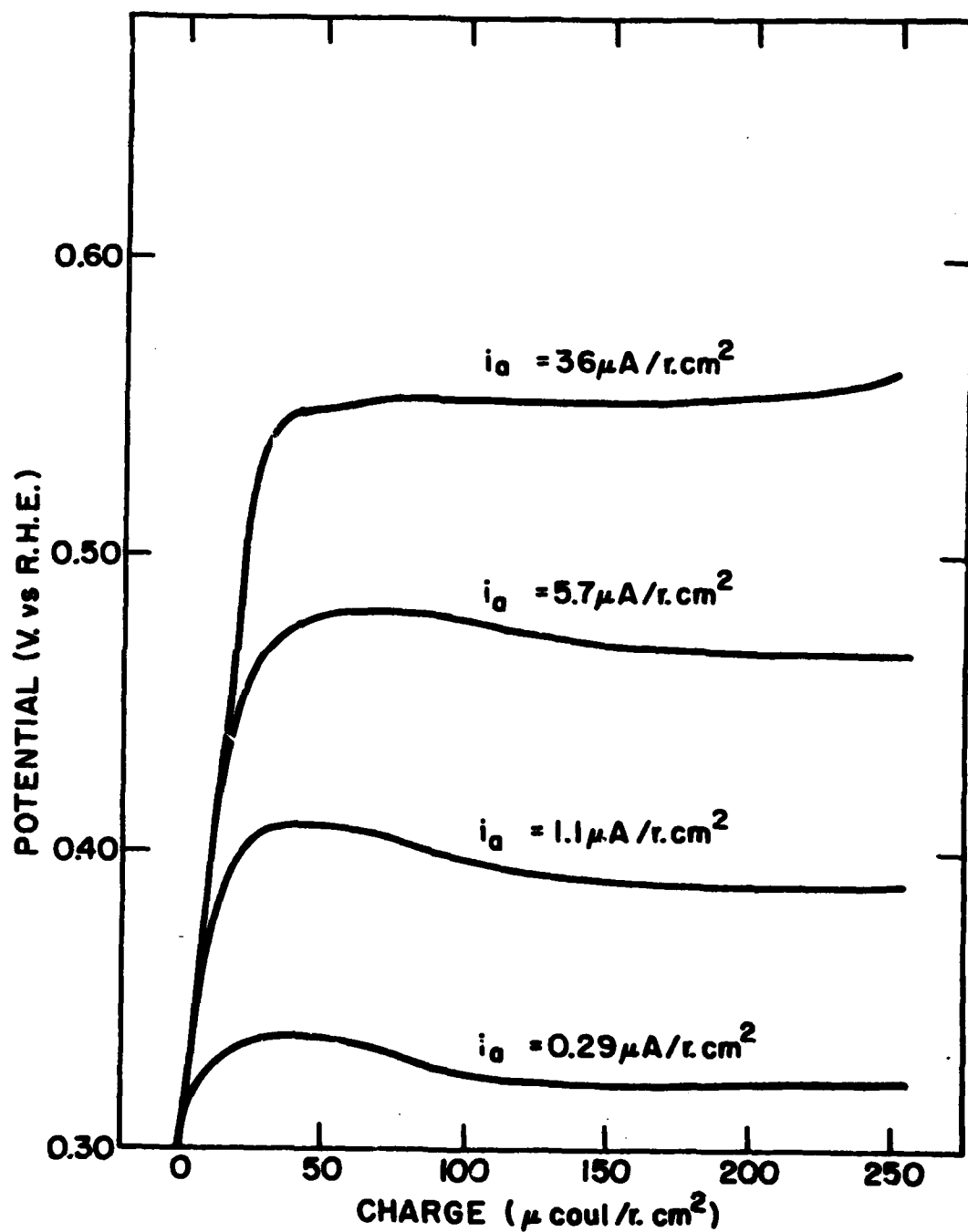


Fig. 14 Initial stripping curve of O-type CH_4 formed at 0.30v as a function of stripping current density.

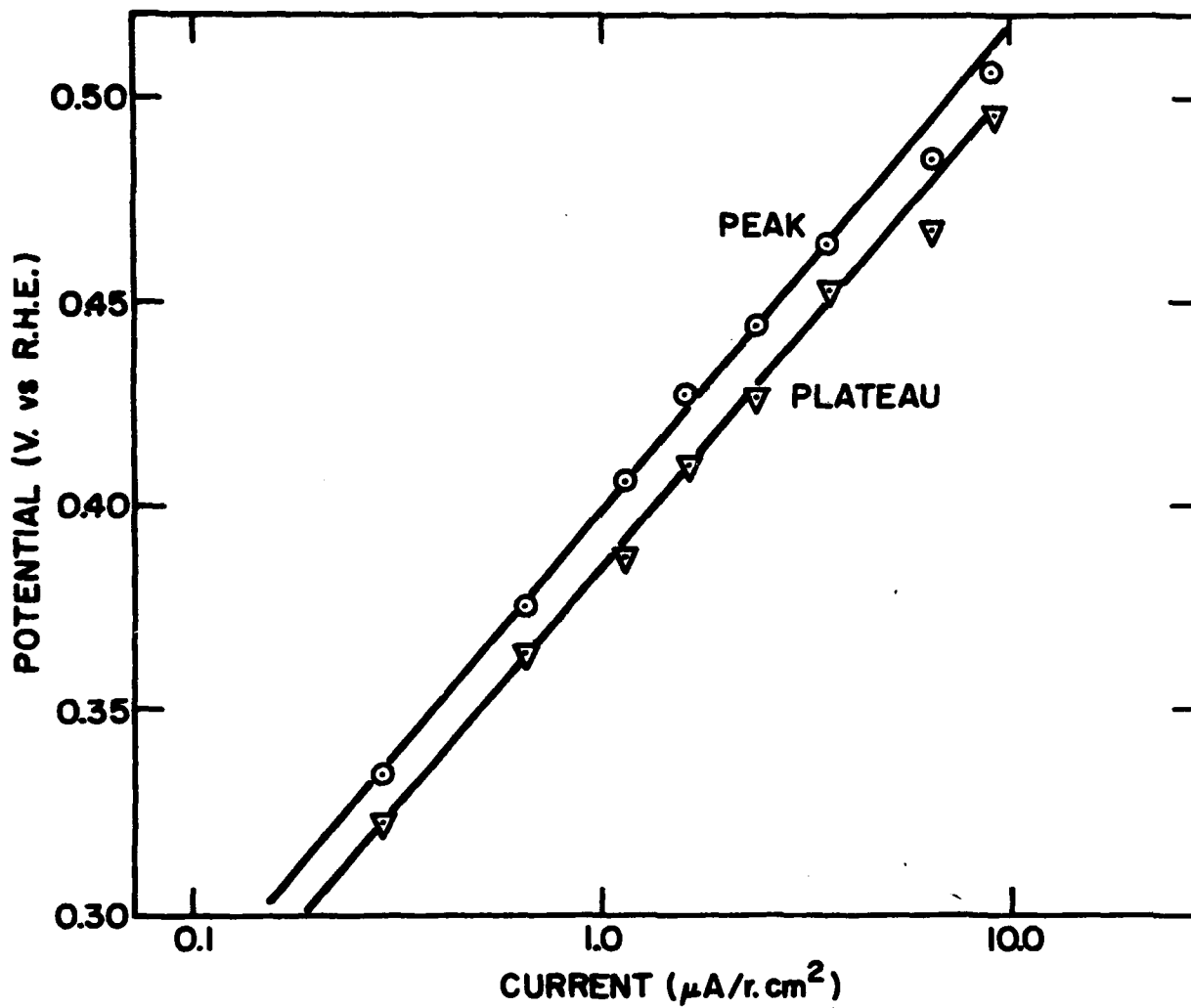


Fig. 15 Initial oxidation potential of O-type CH_4 formed at 0.30v as a function of stripping current density.

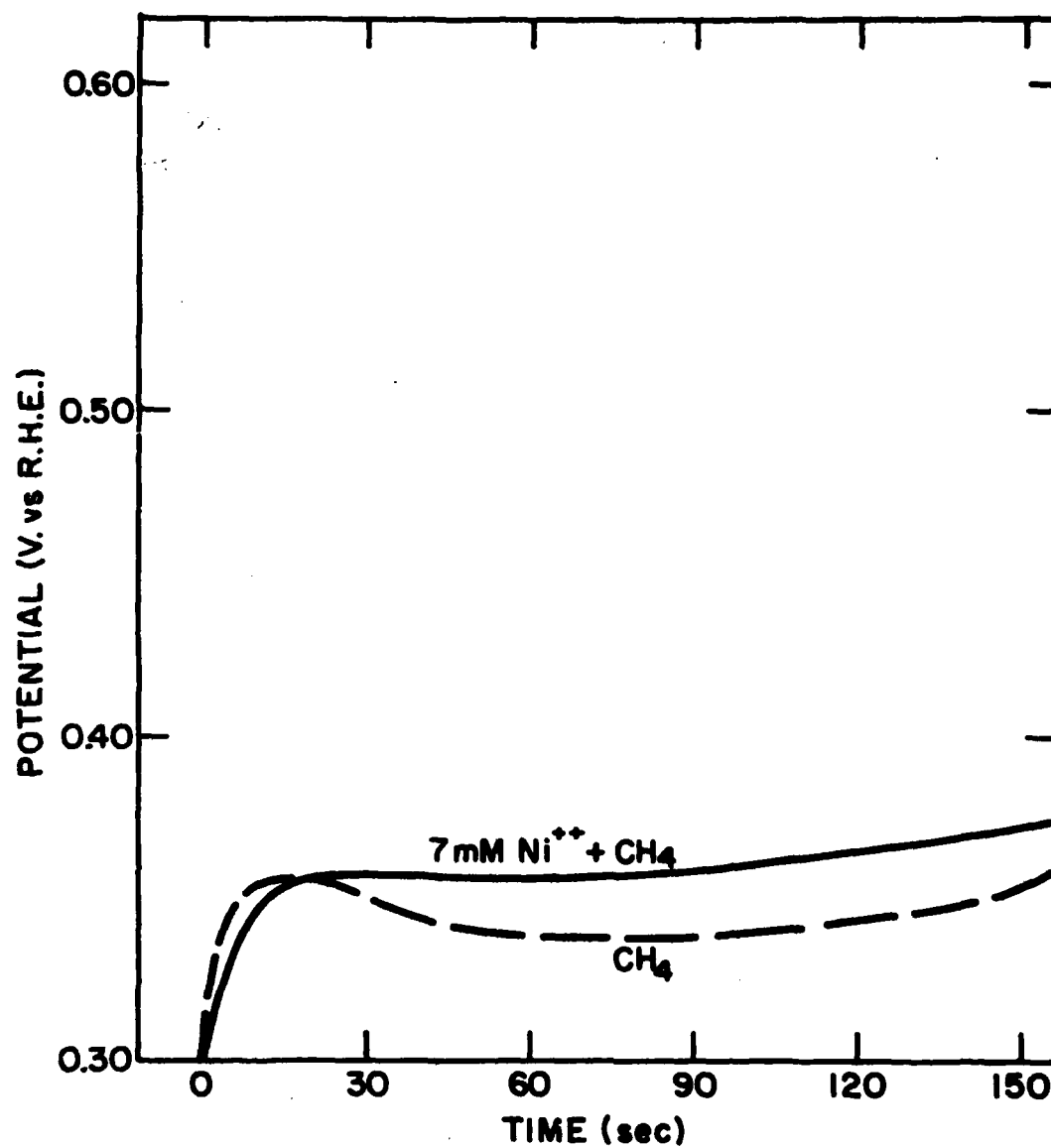


Fig. 16 Effect of 7 mM Ni⁺⁺ on 0.5 μ A/r cm² stripping curve for oxidation of O-type CH₄.

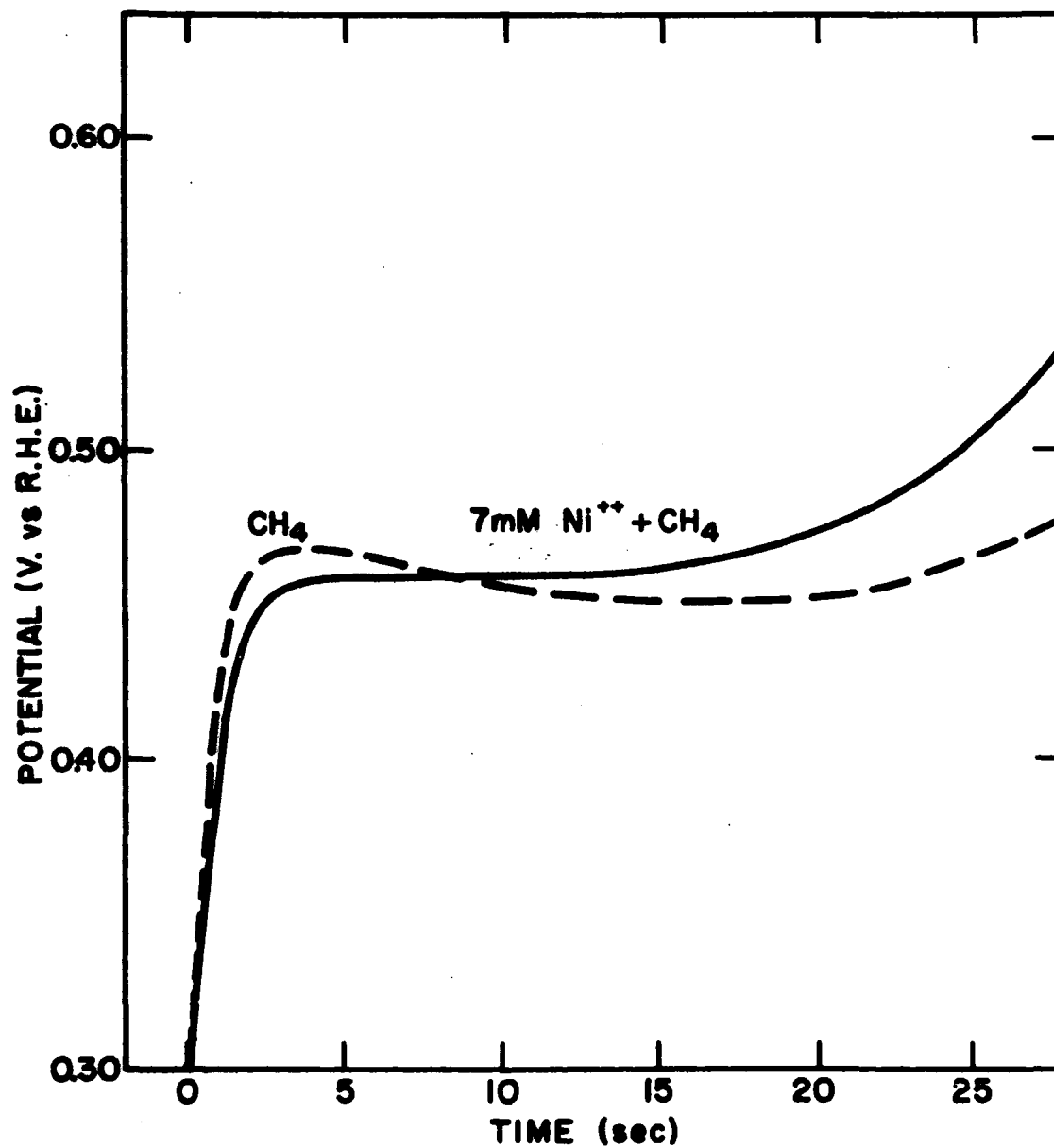


Fig. 17 Effect of 7 mM Ni^{++} on $3.6 \mu\text{A/r cm}^2$ stripping curve for oxidation of O-type CH_4 .

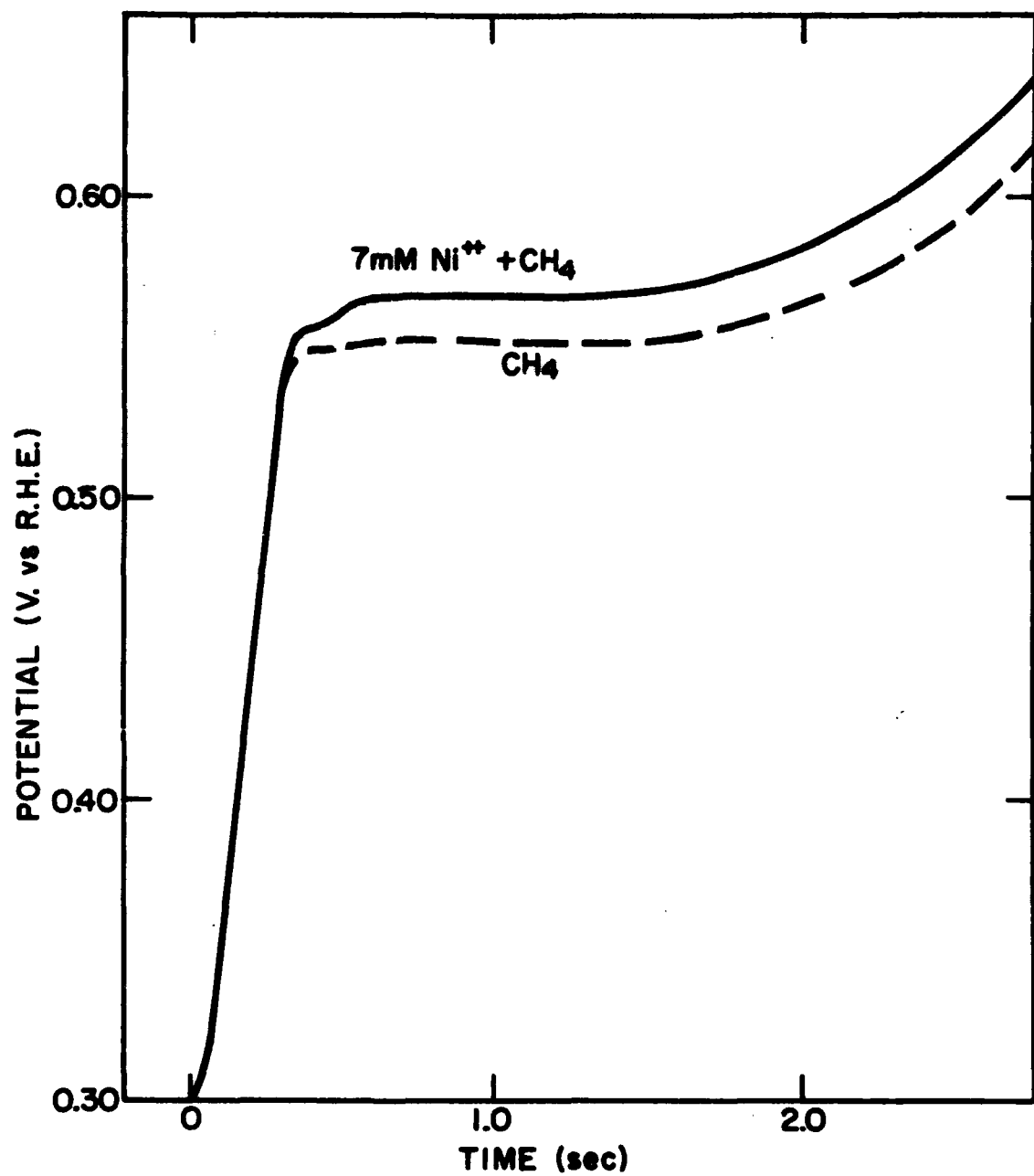


Fig. 18 Effect of 7 mM Ni⁺⁺ on 35.7 $\mu\text{A/r cm}^2$ stripping curve for oxidation of O-type CH₄.

overshoot observed for pure CH_4 completely disappears. The main effect is thus one of inhibition. At $3.6 \mu\text{a/r cm}^2$ the $(\text{Ni}^{++} + \text{CH}_4)$ curve (Fig. 17) again seems to have a shift in the double layer region, suggesting that the oxidation of O-type CH_4 has begun more quickly. As before, there is no overshoot. However, in this case the plateau region does not occur at the CH_4 overshoot potential, as with the lower current density, but rather occurs at some intermediate potential between the peak and plateau of the pure CH_4 data. At $35.7 \mu\text{a/r cm}^2$ (Fig. 18) the 7 mM Ni^{++} just shows inhibition of the oxidation of O-type material. The general character of the two curves is the same, with the Ni^{++} causing a shift of about 18 mv more noble.

The data with a higher concentrations of Ni^{++} , i. e. 250 mM, are even more interesting. The effect of Ni^{++} on O-type oxidation is much more marked, as seen in Fig. 19. This stripping curve, for $1.1 \mu\text{a/r cm}^2$, reveals an initial oxidation which might correspond to adsorbed Ni. The charge is so small ($\sim 10 \mu\text{coul/r cm}^2$) that at the higher current densities used to estimate Ni coverage on smooth Pt it could easily be lost in the double layer region. The rest of the stripping curve shows no real plateau, with the oxidation of O-type being pushed to high potentials.

At this point we should note that we have observed another phenomenon with the higher Ni^{++} concentrations. After pre-electrolysis for 24 hours there was often still some adsorption on the electrode in a N_2 stirred solution. Figure 20 shows the rate of adsorption in a clean CH_4 system and a ("dirty" $\text{Ni}^{++} + \text{CH}_4$) system. Although the total adsorbate charge is higher with a dirty Ni^{++} solution, the initial adsorption rate is much lower. Whatever the impurity in the Ni^{++} solution is, it certainly can inhibit CH_4 adsorption.

If we pre-electrolyze for another 48 hours, there is no more adsorption observed in a N_2 stirred system. Figure 21 illustrates the effect on the oxidation of O-type of 250 mM Ni^{++} which had been pre-electrolyzed 24 hours, designated "dirty", and the same solution pre-electrolyzed 72 hours. At $5.7 \mu\text{a/r cm}^2$, the "dirty" Ni^{++} solution

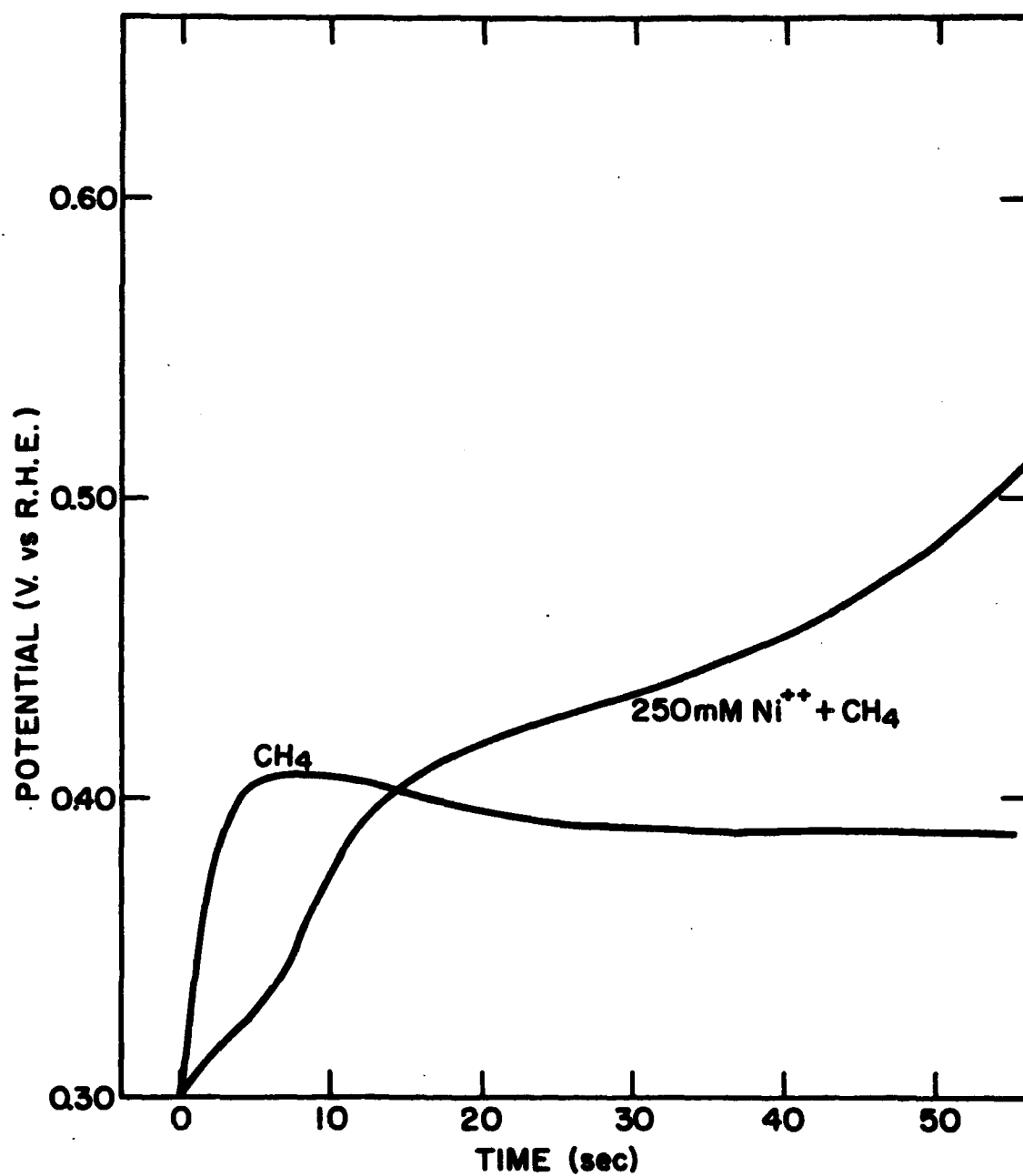


Fig. 19 Effect of 250 mM Ni⁺⁺ on 1.1 $\mu\text{A/r cm}^2$ stripping curve for oxidation of O-type CH₄.

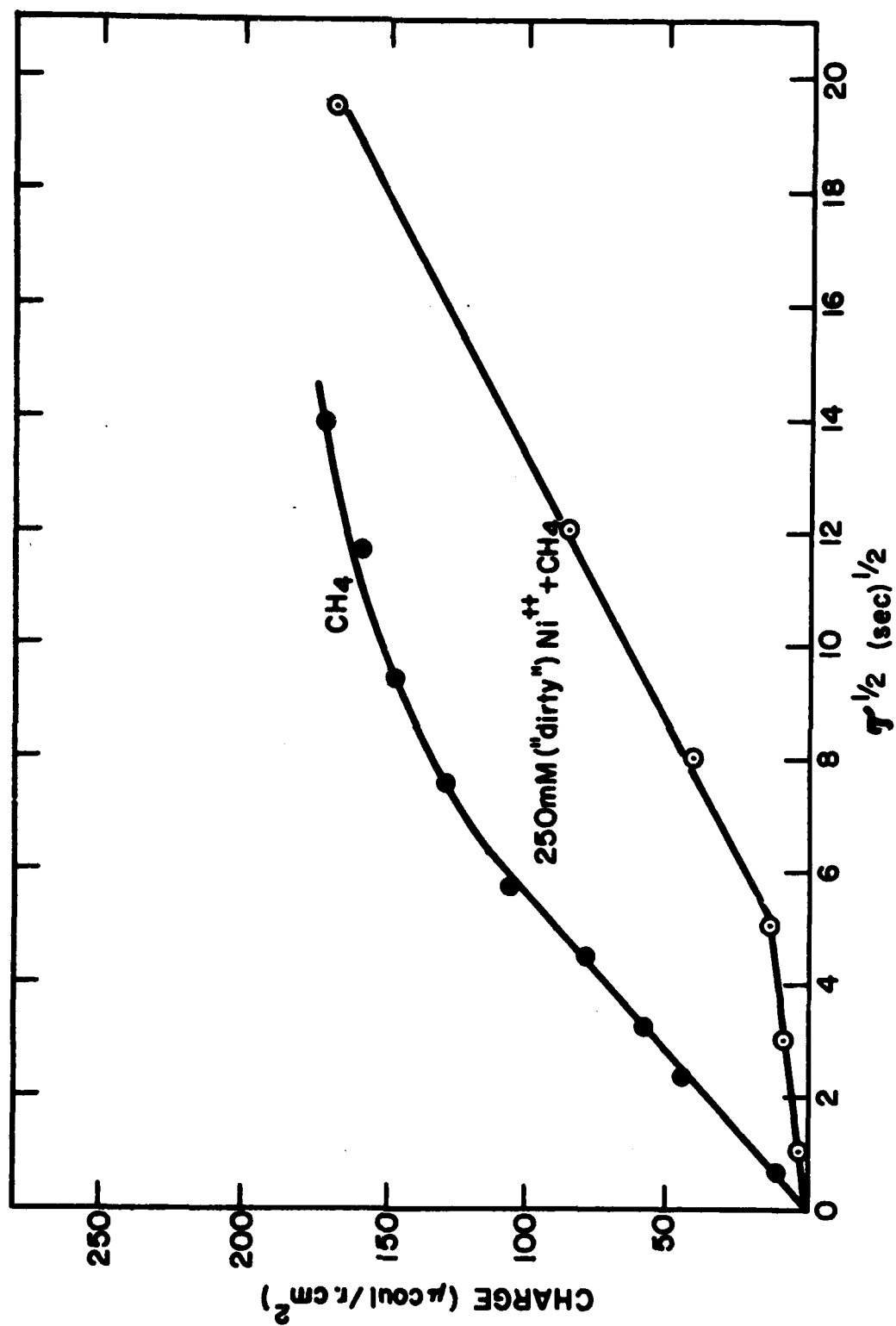


Fig. 20 Rate of charge accumulation without stirring for CH_4 and $(\text{Ni}^{++} + \text{CH}_4)$.

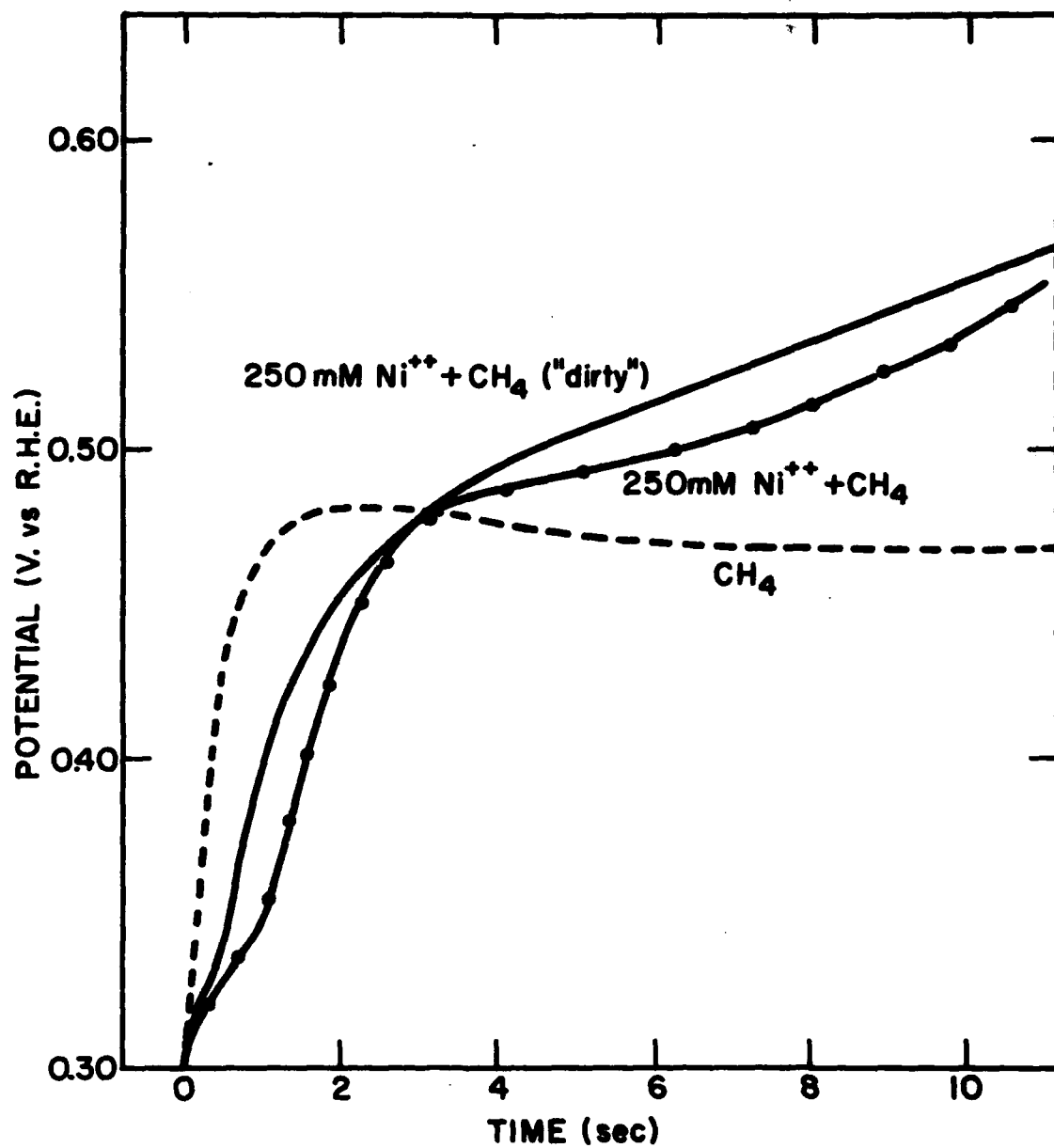


Fig. 21 Effect of 250 mM Ni⁺⁺ solutions on 5.7 $\mu\text{A/r cm}^2$ stripping curve for oxidation of O-type CH₄.

causes a much larger change in mode of oxidation of O-type than does the "clean" solution. At the same time, however, it apparently lowers the initial oxidation potential. The initial wave, which we feel may correspond to adsorbed Ni, is only seen with the "clean" Ni solution. Thus the impurity which we remove by adsorbing on the fuel cell electrode inhibits such adsorption of Ni in addition to inhibiting the low current density oxidation of the O-type material.

In Fig. 22 we see a similar effect with the ("clean" 250 mM $\text{Ni}^{++} + \text{CH}_4$) displaying more character to its O-type stripping curve with a faint suggestion of an arrest. Although these curves were taken at somewhat different stripping current densities for the three situations, they do illustrate that for these high current densities the impurity which we removed enhanced the oxidation of O-type at high current densities, while still preventing the adsorption of Ni. Further study to clarify these effects is clearly important.

The summation of many of these curves is illustrated in Fig. 23. Here we present the initial oxidation potential as a function of stripping current density and concentration of Ni^{++} . Additions of small amounts of Ni^{++} inhibit and shift the potential by the same increment over two orders of magnitude in current. With a "dirty" 250 mM Ni^{++} solution, the curve is skewed, with more inhibition at the lowest current densities and with some enhancement of the oxidation rate at the higher current densities.

In summary, then, the Ni^{++} solutions contain a material which is adsorbed and which may enhance O-type oxidation at high potentials. This material also appears to prevent the adsorption of a small amount of Ni. The low concentrations of Ni^{++} and the high concentrations which have been pre-electrolyzed at least 72 hours inhibit the oxidation of O-type material.

Finally, we have examined the effect of Ni^{++} on the rate of the over-all reaction, $\text{CH}_4 \rightarrow \text{CO}_2$. The aim here was to look for possible effect of Ni^{++} (or the small amount of Ni we may be seeing on platinized Pt) on the rate of reaction (3). The results, in Fig. 24, are very interesting.

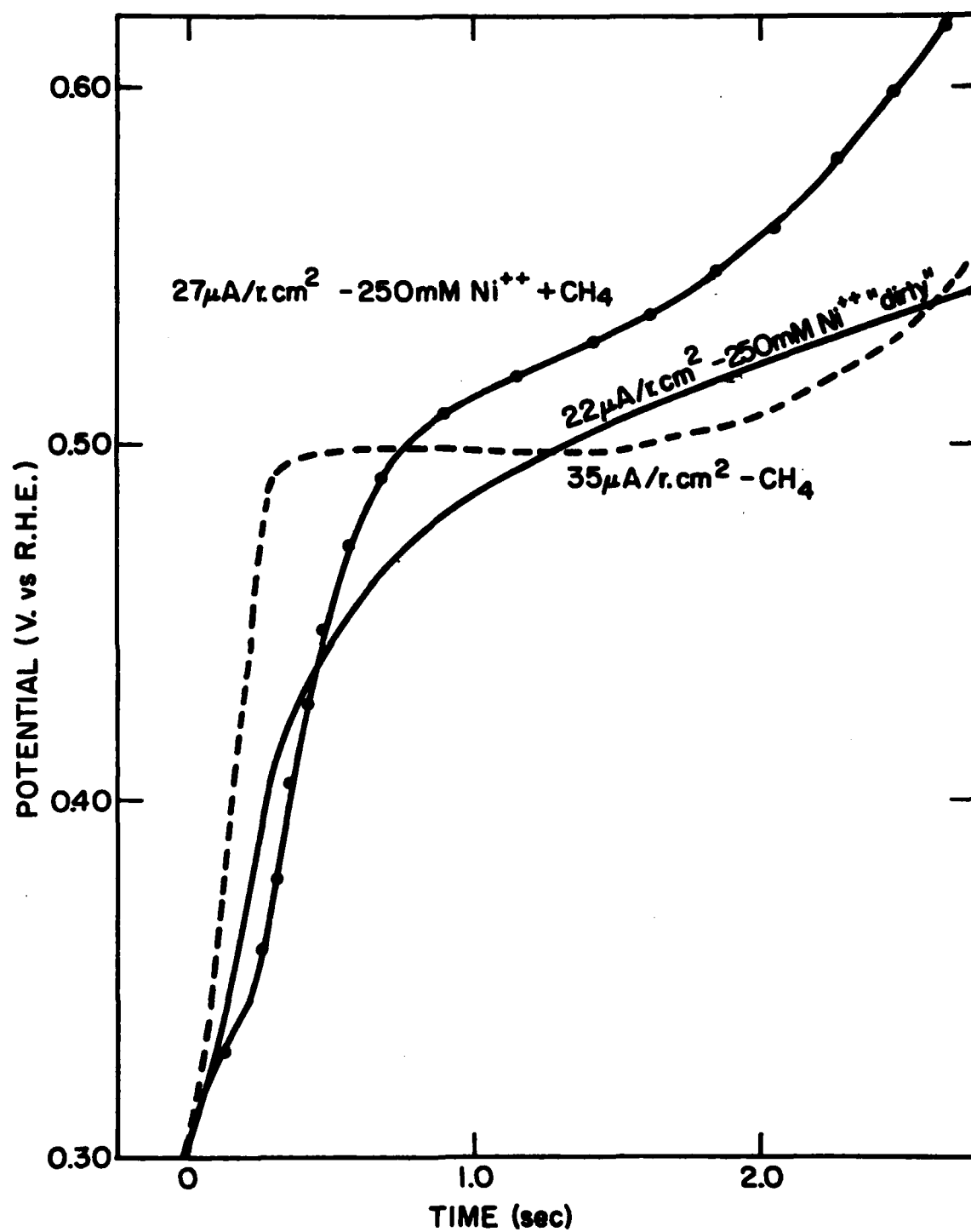


Fig. 22 Effect of Ni^{++} solutions on stripping curves for oxidation of O-type CH_4 .

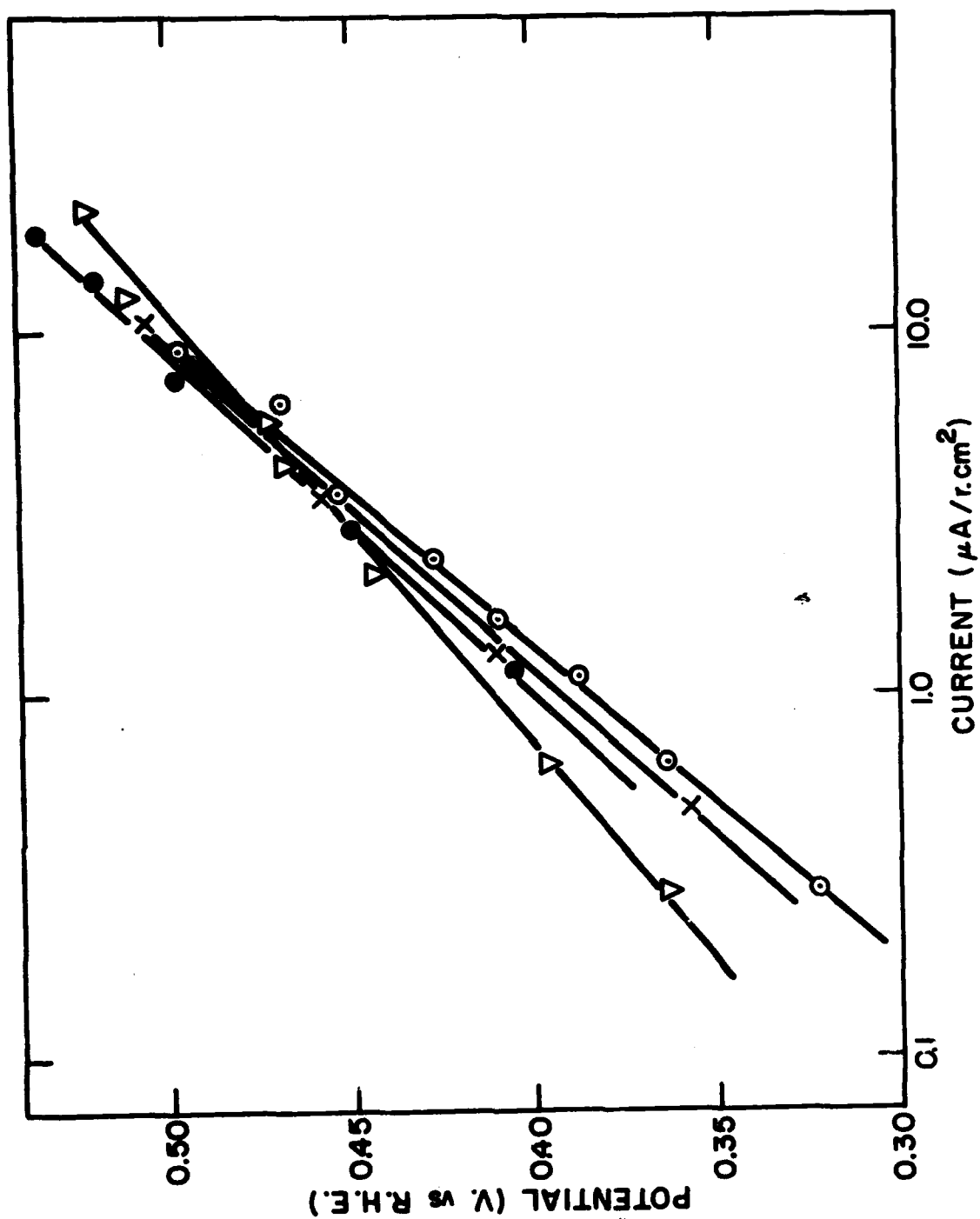


Fig. 23 Initial oxidation potential for O-type CH_4 as a function of stripping current and Ni^{++} in solution (\circ , CH_4 ; \times , 7 mM $\text{Ni}^{++} + \text{CH}_4$; \bullet , 250 mM $\text{Ni}^{++} + \text{CH}_4$; Δ , 250 mM "dirty" $\text{Ni}^{++} + \text{CH}_4$).

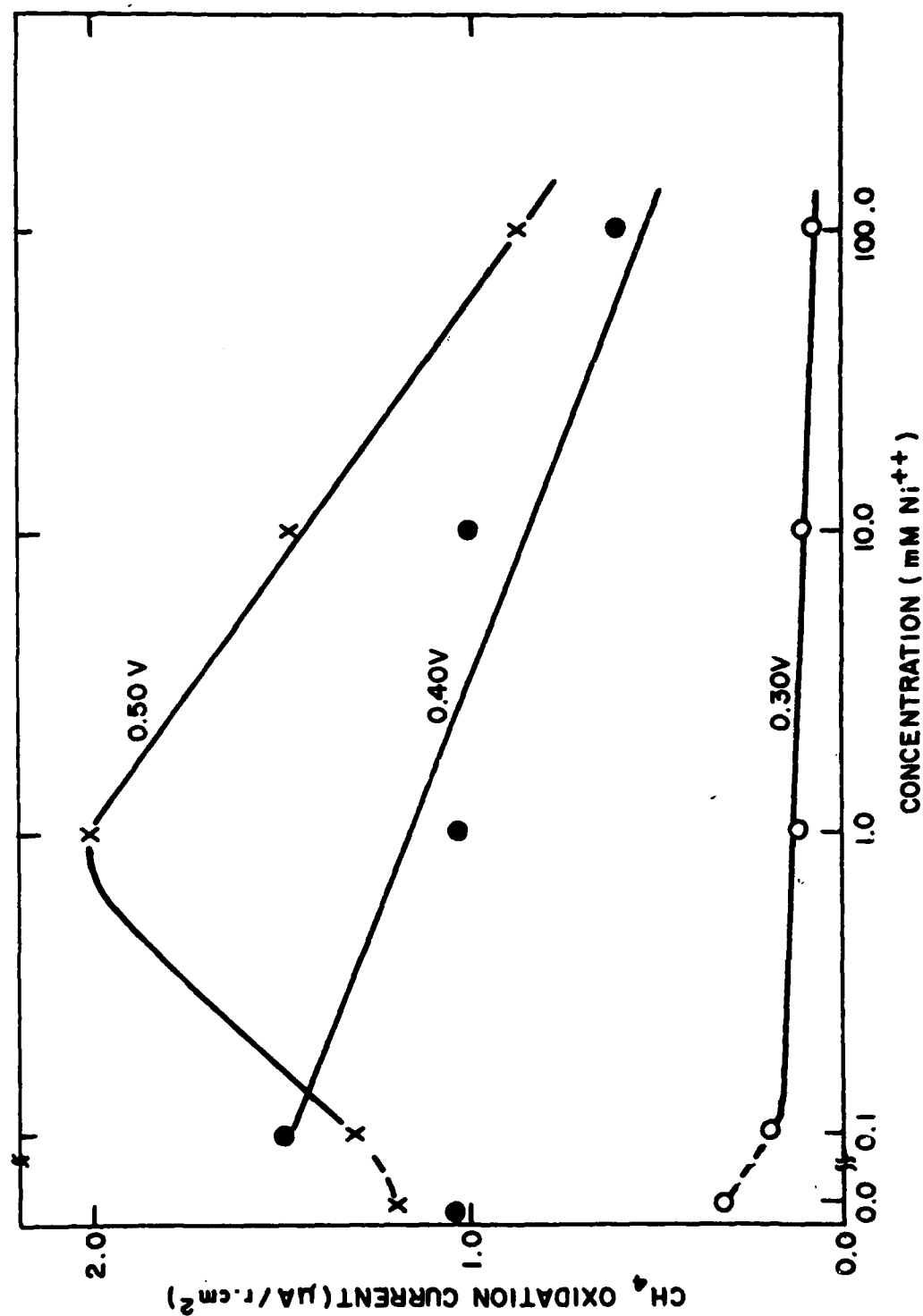


Fig. 24 CH_4 oxidation currents as a function of Ni^{2+} in solution and potential

At 0.30v, where reaction (2) is rate limiting, Ni^{++} is uniformly inhibiting over the whole concentration range from 0.1 to 100 mM. At 0.4v, where both (1) and (3) are important, Ni^{++} in excess of 1 mM also inhibits the reaction. Below this concentration, however, e. g. at 0.1 mM, the over-all reaction is catalyzed by about 50%. At 0.5v, this catalytic effect is even larger (a factor of 2) and appears at a higher Ni^{++} concentration (1 mM). The implication clearly is that Ni^{++} in solution enhances the rate of the adsorption of CH_4 onto Pt. Further work to confirm and to optimize this effect is clearly required.

VI. SUMMARY AND FURTHER WORK

The most interesting result so far is the apparent enhancement of the oxidation of CH_4 by the addition to the solution of Ni^{++} . This effect will be confirmed and, if verified, optimized. In such event, studies will also be made with higher hydrocarbons and with other polyvalent cations, e. g. Co^{+2} , Al^{+3} , Ga^{+3} . Particular attention will be given to experiments designed to explore the likely reason for the catalytic effect. In addition, studies of other cation species, where adsorption of the uncharged atom seems likely, e. g. Ag, Pb, will be undertaken. The aim here, in particular, is to look for a metal which will catalyze the oxidation of O-type.

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<p>The oxidation of CH_4 on Pt electrodes in 80% H_3PO_4 at 130°C has been studied. Emphasis has been put on the development of non-noble metal catalysts. To prevent corrosion the approach has been to stabilize these catalysts by adsorption. Studies were made of the adsorption of Cu from solutions containing Cu^{++}. Cu adsorption on Pt is controlled by the rate of diffusion of Cu^{++} to the Pt electrode. Appreciable steady state coverage of Cu is found at potentials anodic to the reversible potential for the Cu^{++}/Cu reaction, proving that adsorption of Cu does occur. Maximum adsorption (about 0.8 of a monolayer) is found at about 0.20v vs. the reversible hydrogen electrode (RHE), with a slow decline to zero coverage at ~0.60v. The effect of Cu^{++} concentration on the coverage is most marked in the lower potential range from 0.10 to 0.35v.</p> <p>Comparisons of the charge to oxidize the Cu layer, Q, with its coverage, θ, allow evaluation of the number of electrons released per site when the layer is oxidized, $[e]$. It is found that the $[e]$ value for the first half of the monolayer coverage is 1.8 electrons per site independent of potential. This corresponds closely to the value expected for the oxidation to Cu^{++} of singly bonded Cu atoms on the surface. For $\theta > 0.5$, the $[e]$ value becomes significantly larger, particularly at lower potentials, which suggests incipient metal crystalline formation at these coverages.</p> <p>CH_4 adsorbs on Pt in the presence of Cu. In general, the charge to oxidize a combined (Cu + CH_4) layer is greater than that to oxidize either of the two separately produced layers, but far less than the sum of the charges to oxidize these two individual layers. Measurements of the $[e]$ value for the combined (Cu + CH_4) layer</p>			

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show that coverage with CH_4 species is unchanged in presence of Cu. This suggests that the Cu modifies the rates of formation and oxidation of the CH_4 layer in the same proportions. Studies of the effect of Cu on the over-all reaction of CH_4 to CO_2 show an inhibiting effect, which is the same over the whole potential region of interest from 0.30 to 0.60v. The reaction mechanism changes in this potential region such that at the low potentials the rate limiting step is the oxidation of the adsorbed species (O-type), and at the high potentials it is the initial adsorption of CH_4 . Apparently, the Cu diminishes the rates of both of these reactions equally, but most likely by a simple area effect.

→ The adsorption of Ni from solutions containing Ni^{++} has been studied with smooth and platinized Pt electrodes. Even with very pure sources of Ni there appears to be some adsorption on the Pt. However, with an extensive adsorptive pre-electrolysis it has been shown that Ni does not adsorb appreciably on smooth Pt in the potential region of interest and that the bulk of the adsorption observed is due to minor impurities in the originally very pure Ni. On platinized Pt a minor oxidation wave corresponding to about $10 \mu\text{coul/cm}^2$ ($< 5\%$ of a layer) is observed which may correspond to the oxidation of a small amount of adsorbed Ni. It has been observed that the minor impurity carried with Ni kinetically inhibits CH_4 adsorption.

→ Studies were made of the effect of Ni^{++} on the oxidation kinetics of CH_4 and on the oxidation kinetics of O-type CH_4 . O-type oxidation exhibits the following features: Initially, on the application of a current the potential rises until the oxidation process starts. This potential varies with the applied current. After the removal of a small fraction of the adsorbed O-type the potential decreases, giving rise to an initial peak in the galvanostatic stripping curve. Subsequently a long plateau, where the potential scarcely changes with time, is observed until almost all of the O-type has been oxidized. At this time the potential starts to rise again.

→ Small concentrations of Ni^{++} in solution caused profound changes in the shape of the Q-type stripping curve. At low currents the initial oxidation of O-type appears to begin more quickly in presence of Ni^{++} , but the potential at which most of the material is stripped is higher and the potential overshoot normally observed completely disappears. The main effect is thus one of inhibition. At high currents the preliminary apparent enhancement of rate does not appear and some inhibition (at least 20 mv at fixed current) is observed over the whole stripping curve. With very high concentrations of Ni^{++} , e.g. 0.25 M, the behavior depends on how well the solution is pre-electrolyzed. Interestingly, it appears that the impurity carried with Ni^{++} (Co^{++} ?) enhances the oxidation of O-type, particularly at high current densities, and prevents what appears to be a minor adsorption of Ni.

The oxidation potentials are a linear function of the logarithm of the current density. For O-type formed in absence of Ni^{++} , the plateau potential-current relation has a slope of 116 mv/decade. The peak potential-current relation has a slope of 109 mv/decade suggesting that the process

corresponds fairly closely to the transfer of 1 electron from O-type to the electrode. These potentials are shifted by the addition of Ni^{++} to the solution. Small concentrations of Ni^{++} (7 mM) merely shift the current-potential curve for the initial oxidation of O-type in the noble direction but do not appear to change the Tafel slope. A very concentrated Ni^{++} solution which has not been completely purified by pre-electrolysis causes a change in the Tafel slope with a greater inhibition of the process at low current densities but some enhancement of the process at very high current densities.

Ni^{++} in solution catalyzes the over-all CH_4 to CO_2 process. The extent of this catalysis varies with potential. At 0.30v, where O-type oxidation is rate limiting, no catalytic reaction is observed. At 0.40v the reaction rate is enhanced by about 50% for a Ni^{++} concentration of 0.10 mM. Above 1 mM Ni^{++} inhibits the over-all reaction at this potential. At 0.50v a 1 mM solution enhances the reaction by a factor of 2, but higher concentrations cause inhibition. The results appear to show that Ni^{++} enhances the rate of adsorption of CH_4 and hence its rate of oxidation.

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